UNDERSTANDING THE EFFECT OF NANOKAOLINS ON THE PHYSICAL AND MECHANICAL PROPERTIES OF NYLON BASED COMPOSITES

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UNDERSTANDING THE EFFECT OF NANOKAOLINS ON THE PHYSICAL AND MECHANICAL PROPERTIES OF NYLON BASED COMPOSITES

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To my Parents, for helping me get this far

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LIST OF SYMBOLS AND ABBREVIATIONS

FRP	Fiber Reinforced Plastic
PA6	Nylon 6
PA66	Nylon 66
SEM	Scanning Electron Microscopy
XRD	X-Ray Diffraction

SUMMARY

Kaolin minerals are increasingly being used as “Performance Minerals’ in polymer composites due to the promising benefits that they provide in terms of mechanical performance. Due to the downsides of the current state of the art in glass fiber reinforced plastics, kaolin minerals are considered as a potential substitute to glass fibers. This thesis investigates the use of different kaolin formulations in a nylon 6 and a nylon 66 polymer matrix and analyzes the potential benefits on the mechanical properties of the composites. The minerals themselves vary in terms of surface treatment, particle size and aspect ratio. The composites are produced using a lab scale twin screw micro-extruder and injection molding machine. The mechanical properties including tensile and flexural modulus and strength and impact strength of the composites are determined as a function of the kaolins’ characteristics. In addition, XRD and DSC characterizations are performed to better understand the effect of the kaolins on the crystallization behavior of the nylons and investigate potential synergistic effects of the kaolins that is whether or not they alter the physical properties of the nylons in addition to enhancing their mechanical performance. SEM imaging is also performed to investigate the distribution of the mineral within the polymer matrix. It is concluded that smaller particle sizes lead to a better tensile and flexural performance while higher aspect ratios lead to stiffer composites. Due to the nano-size kaolin particles, there is inevitable agglomeration as shown in the SEM study. The mechanical performance demonstrated by the kaolin incorporated composites prove that kaolins can replace glass fibers while providing additional benefits such as better surface finish.

INTRODUCTION

1.1 Background

Thermoplastic composites have been gaining widespread popularity in multiple industries throughout the world. Not only do they provide the benefits of having higher strength- and stiffness-to-weight ratios than metals but can also be cost effective, especially when used in the automotive industry. A 100kg weight saving in a car results in about 0.7L of saved fuel per 100km [Reynolds et al.], hence providing a strong incentive for industry and governments alike to switch to such composites as it can benefit the environment and lead to a more sustainable future. Thermoplastics also benefit from the fact that there are a countless number of them, ranging from acrylics to polyesters and polyamides. This allows them to be used in a wide variety of applications by allowing engineers and scientists a high degree of flexibility. This flexibility also allows for changing the physical and chemical properties of the thermoplastics, suiting them to whatever need is required.

Thermoplastics in their current form originated in the early 1920s when PVC was plasticized by Waldo Semon and the B.F. Goodrich Company [Smith]. This process led to a much easier handling of the material and made it much more suitable for commercial applications such as pipes. Over the years, there was a strong growth in the discovery and invention of new plastics. By the 1970s, a new field named ‘Engineering Thermoplastics’ had been founded that focused exclusively on the applications of thermoplastics in high performance settings. From this began the use of thermoplastics in the aerospace and automotive industries in the form of composites, where thermoplastics formed a base matrix and were combined with various reinforcements for structural strength. Initially,

composites were mostly used for weight reduction purposes and carried non-structural loads. However, with advancements in technology, thermoplastics composites can now be used for virtually any component, from a monocoque chassis of a car to the wings of an aircraft. The relative weight of composites as compared to metals and other materials are shown in Table 1 [MacKenzie et al.].

Table 1 Relative weight savings of composites

Material	Relative Weight Savings
Conventional Steel	0%
Iron	0%
High-Strength Steel	23%
Aluminum	45%
Magnesium	60%
Plastics & Composites	50%

Composites are mainly used when light-weighting of a component/structure is required. Biron highlights that the mean savings by using plastics is around 48%, which is significant [Biron]. It is clear why many automotive firms are continuing to choose composites as their primary materials choice. It is also estimated that making composite

parts out of thermoplastics can reduce manufacturing time by 25-30% [Reinforced Plastics]. Some of the other advantages of thermoplastic composites include:

- Lightweight (with densities between 0.9 and 2 g/cc)
- High strength-to-weight ratio
- Low processing cost and hence high volume production
- Ability to be reheated, melted and reformed multiple times
- Ability to withstand larger deflections than metals

While thermoplastics come with a large number of benefits, they also have a few disadvantages. Firstly, thermoplastic composites tend to fracture instead of deforming under high stresses, unlike metals [Girard]. Depending on the application, this may not be suitable and can lead to catastrophic failures. They also have a much lower melting temperature than metals and can degrade upon exposure to UV light and organic solvents.

Although thermoplastic composites provide numerous benefits on their own, their properties can still be further enhanced by the addition of fillers. Fillers are particles, usually in the micro and nano scale, that can improve certain characteristics of a thermoplastic matrix. Amongst other reasons, fillers can help mitigate some of the composites' disadvantages mentioned above. Furthermore, they can help reduce costs of production since they are generally cheaper than the matrix itself [Mallick, Chapter 2]. Inorganic particulates, such as kaolins and carbonates, when added to the resin can improve some mechanical properties of the thermoplastic composite such as modulus as shown in Table 2 . The most common types of fillers in thermoplastic composites are mineral fillers, which include carbonates, kaolin, talc, mica and glass microspheres [Mallick, Chapter 2].

Many of the minerals are mined and an example of a kaolin deposit can be seen in Figure 1.

Table 2 Effects of fillers on mechanical properties of polymers

Property	Unfilled Polyester	Polyester filled with 30 phr $CaCO_3$
Density (g/cm^3)	**1.3**	**1.48**
HDT (°C)	**79**	**83**
Flexural Strength (MPa)	**121**	**62**
Flexural Modulus (GPa)	**4.34**	**7.1**

1.2 Kaolin As A Filler In Thermoplastic Composites

Kaolin is a rock commonly found in soils in regions where the climate is moist and warm and is produced from the weathering of other rocks. The clay mineral, kaolinite, is mined from these rocks and produces a soft, whitish appearance [Murphy]. It has the chemical structure $Al_2Si_2O_5(OH)_4$ and has a plate like structure as shown in Figure 2.

Figure 1 A kaolin mine in Cantarrana, Bolivar state [Sousa]

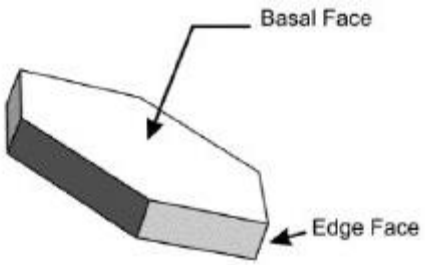

Figure 2 Plate like structure of kaolin [Narra]

In industry, more than half of the kaolin use is accounted for in paper manufacturing, where it used as a coating agent and provides paper its white texture and appearance. Since it acts as a filler, it helps reduce costs for the industry while also lowering consumptions of natural resources in paper production. Historically, kaolin was mostly used in the production of chinaware and porcelain due to its glossy appearance and hardness, however, today this industry does not account for significant consumption of

kaolin. Some other industries where kaolin is used are cosmetics, paints and medicine [PubChem].

Minerals such as kaolin are being classified today as ‘Performance Minerals’ since they have the ability to alter the mechanical properties, such as stiffness and impact strength, of the final composite while also helping to reduce cost. Depending on the requirements, the minerals can be altered to produce different particle sizes and surface treatments that can modify the composite in the desired manner. Figure 3 showcases some of the various kaolins produced by Imerys, a multinational minerals company. Some of the applications where kaolin minerals produced by Imerys are used are wheel and engine covers, instrument panels, cooling fans, tooling and appliance parts [Engineering Thermoplastics].

In general, smaller particle size tends to lead to an increased impact strength [Onuegbu et al. 2011]. Particle shape also tends to affect the mechanical properties with plate like structures leading to higher tensile and flex modulus. Another important property of the mineral is its aspect ratio, which is defined as the ratio between the particle’s longest side to its shortest side. Kaolin particles come in a wide variety of shapes and can hence have a large variation in the aspect ratio. A study done by Wiebking revealed that an increase in the aspect ratio tends to lead to higher stiffness. These facts will be further evaluated during the mechanical testing in this study. Figure 4 shows the difference in physical properties between calcined and non-calcined kaolin, as provided by Imerys.

PHYSICAL CHARACTERISTICS

Grade	Brightness (GE % of MgO)	Mean particle size (Sedigraph) (µm)	Applications
PoleStar® 450HP	85	1.0	High performance MetaKaolins for low voltage PVC cable compounds
PoleStar® 450	85	1.5	
PoleStar® 503S	90	1.2	Functional pigment for EPDM medium and high voltage cable insulation
Hydrite® TS90	91	0.2	Super ultra fine hydrous clay for improved TiO_2 spacing in white polyolefin masterbatch
Hydrite® SB 100	86	1.2	Hyper platy clay in Barrier applications | Inner liner tire applications
PoleStar® 400	92	0.6	Ultra fine calcined kaolin for Greenhouse films
Glomax™ LL	91	1.5	Reinforcing filler for seal and gasket applications
Polarite® 404S	92	0.6	Specialized kaolin for silicone rubber applications
Hydrite® SB 60	88	0.4	Hyper platy clay in Barrier applications | Inner liner tire applications
Polarite® 902A	86	1.4	Innovative reinforcing surface modified kaolins for polyamide and other engineering alloys/composites
Polarite® 502A	91	1.2	
Hydrite® KC	86.5	0.4	High brightness and color consistency functional kaolins for rubber compounds
Polarite® 403A	91	0.6	

Figure 1 Imerys Performance Kaolins and their Applications [Imerys]

QUICK VIEW

Kaolin	
Typical Aspect Ratio:	5:1 /100:1
Specific Gravity:	2.6
Refractive Index*:	1.56
MOH Hardness*:	2.5
Moisture: (max %)	1.0
pH:	4.5 - 7.0

Calcined Kaolin	
Particle Shape:	Irregular, with surface voids
Specific Gravity:	2.6
Refractive Index:*	1.56
MOH Hardness*:	4-5
Moisture: (max %)	0.5
pH:	6 - 7.5

*The data quoted are determined by the use of IMERYS Minerals Ltd Standard Test Methods

Figure 4 Effects of surface treatment on kaolin properties [Imerys]

1.3 Nylon In Composites

In 2017, the worldwide production of plastics was more than 350 million metric tons and the total production is expected to hit more than 1.8 billion metric tons by 2050 [Qualman]. This fast growing trend can be seen in Figure 5. From these plastics, nylon 6 (PA6) and nylon 66 (PA66) together accounted for almost USD 25 billion in sales in 2016 and continue to grow at 6.1% annually with an ever increasing emphasis on automotive and engineering plastics industries as shown in Figure 6.

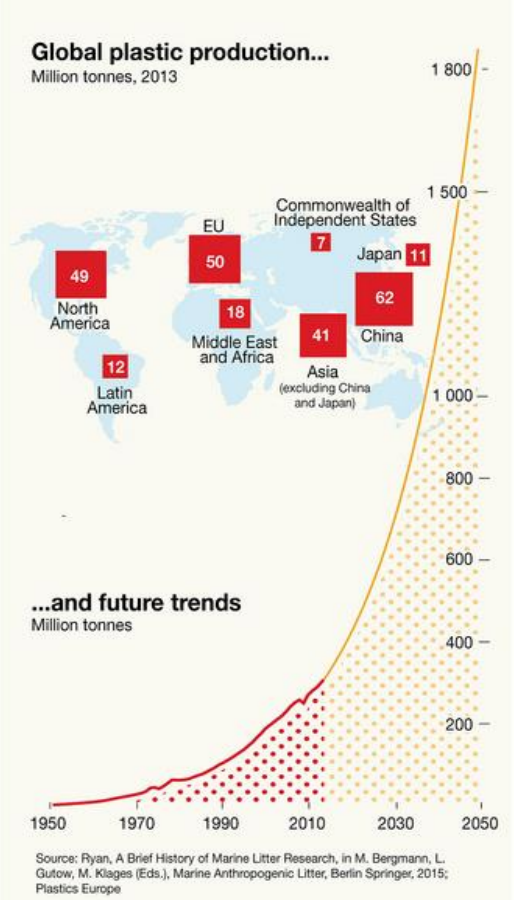

Figure 5 Global production of plastics [Qualman]

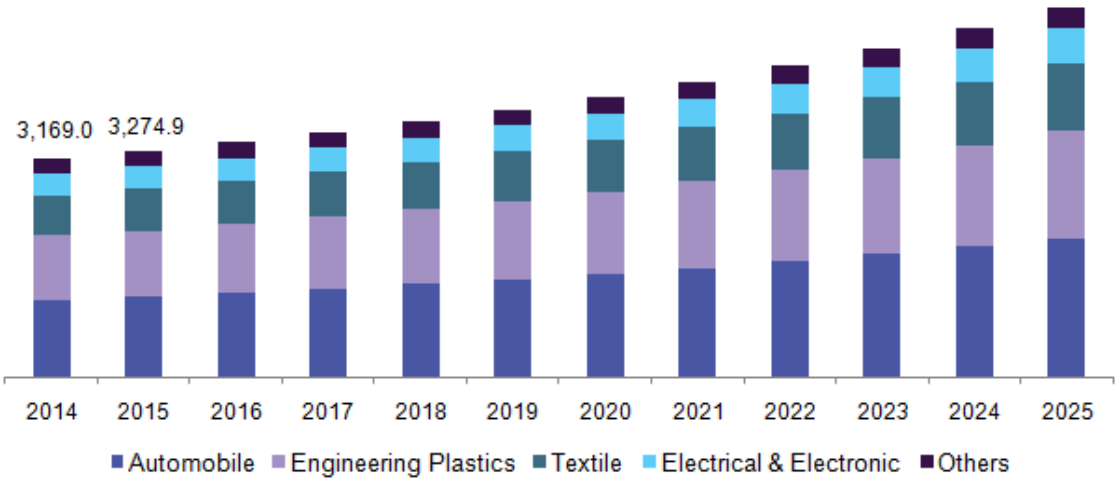

Figure 6 US market revenue from nylon 6 and nylon 66 [Grand View Research]

The strong global market forces of supply and demand are leading to ever increasing use of these polymers. In global nylon market, 60% of the demand is captured by nylon 6. In the automotive industry alone, an average of 11 lbs. of nylon 6 is used in the production of each vehicle and this number is set to grow [Grand View Research]. Nylon 66 is also growing in terms of demand due to its vast engineering applications. The key differences between the two polymers are outlined in Table 3.

Table 3 Comparison of nylon 6 and nylon 66 properties [Ai Engineering Plastics and Laminates]

NYLON 6	NYLON 66
Less crystalline	More crystalline
Lower mold shrinkage	Exhibits greater mold shrinkage
Lower melting point	Higher melting point
Lower heat deflection temperature	Higher heat deflection temperature
Higher water absorption rate	Lower water absorption rate
Poor chemical resistance to acids	Better chemical resistance to acids
Withstands high impact and stress and better stands up to hydrocarbons	Better stiffness, tensile modulus and flexural modulus
Lustrous surface finish, easy to color	More difficult to color

Polyamides provide many attractive properties that make them a suitable resin for composite materials, including high toughness over a large range of temperature, high impact strength and resistance to organic solvents. However, performance can be limited by degradation during processing. According to Whitfield et al, glass fiber reinforced PA6 composites showed inferior properties after being put through multiple injection and extrusion cycles. The reduced properties mainly contributed to high amounts of mechanical shear stresses present within the extruder and the decreased molecular weight of the polymer chains. It is important to note these mechanisms as the main cause of degradation for the PA6 in this study is due to thermal and oxidative effects during the compounding and injection processes.

Due to an ever-increasing demand for nylon products, there is an ever increasing need to find better performing composites using different base polymer matrices. Since nylon 66 also provides many of the benefits of nylon 6 in addition to the withstanding higher temperatures and being mechanically stronger, it will also be analyzed as a potential substitute for nylon 6 in this study.

1.4 Fiber Reinforced Plastics

Fiber reinforced plastics (FRP) are in widespread use today thanks to advancements in technology as well as economies of scale. The composites comprise of fibers (usually carbon or glass fibers) that give the composite its mechanical properties, along with a matrix usually made of a thermoplastic or thermoset resin such as nylon 6 or epoxy. Due to their high strength-to-weight ratios, FRP are commonly being used in structural

applications in industries such as construction and automotive. Furthermore, they are also immune to degradation due to rust and other issues that are present in metals.

However, they do have some downsides. FRPs, especially carbon and to some extent kevlar, are often much more expensive than their metal counterparts. This is due to the way the fibers must be manufactured. Cheaper alternatives are glass fibers, which are easy to manufacture in the form of chopped strand mat and can be used with thermoplastics in manufacturing methods, such as injection molding. This allows a much cheaper running rate along with high volume productions, but their mechanical performance cannot be compared to that of carbon or kevlar composites.

There are other issues as well. Fiber reinforced plastics can be difficult to repair once they begin to fail. Furthermore, it is difficult to recycle them and they can negatively impact the environment. On the manufacturing side, there are multiple barriers, such as damage to equipment and machinery due to the abrasive nature of glass fibers. This leads to higher costs for manufacturers and the industry as a whole due to constant tool and machine replacement costs. Fillers, such as kaolin, can potentially solve these issues by replacing glass fibers. While their densities are similar (2.65 g/cm^3 for kaolin vs 2.55 g/cm^3 for glass fibers), kaolins can provide a much better surface finish with less abrasion while also providing similar mechanical properties as glass fibers.

1.5 Problem Statement And Motivation

Glass fibers are widely used in thermoplastic composites and continue to replace metal and other components in various industries. However, they pose drawbacks in the form of their abrasive nature which can damage manufacturing equipment leading to higher

costs. The research done previously by Baioumy [Baioumy] on the use of kaolin fillers in glass fiber/ nylon 6 composites showed promising results. Glass fibers replaced with kaolin showed similar mechanical properties with high impact strengths. Building on Baioumy's findings, this thesis continues to understand the effects of surface-treated kaolin mineral fillers with varying morphologies to replace or reduce the weight percentage of glass fibers in nylon composites. The methodology will mimic that used by Baioumy and will focus on the use of a lab scale production since it was determined that the lab scale twin screw compounder replicates scaled-up manufacturing well. This study will further analyze the effects of introducing compatibilizers into the composites and determining the additional benefits of adding them. Lastly, as outlined earlier, the polymer matrix will be also be changed from nylon 6 to nylon 66 and the mechanical properties will be evaluated. This will help in getting a better insight into the potential of using kaolin fillers in nylon 66 and any additional benefits derived from them.

1.6 Goals And Objectives

The aim of this study is to build on upon prior work that investigated the feasibility of using surface treated in a glass fiber/ nylon 6 composites with the aim of potentially reducing or eliminating the use of glass fibers [Baioumy]. Research done by Baioumy suggested high aspect ratio kaolin minerals reach up to 80% strength and modulus of glass fiber composites. By introducing different types of kaolins, this study will investigate 3 major aspects of the kaolin-nylon composites: Specifically it will determine the

1. The effect of introducing different kaolins into a nylon 6/glass fiber matrix on the mechanical properties of the composites

2. The effect of introducing compatibilizers into nylon 6/kaolin/glass fiber composite
3. The effect of substituting glass fibers with kaolins and changing the polymer base from nylon 6 to nylon 66

These objectives will be achieved by means of fabricating composite samples using a lab scale twin screw micro extruder and injection molding machines. The composites will be manufactured with varying weight percentages of polymer matrix, glass fibers, kaolin and compatibilizers and the exact formulations will be outlined in the following chapter.

In each phase of the study, the tensile, flex and impact properties will be determined and compared with a benchmark to better understand the effects of the addition of kaolin. The benchmarks will include pure nylon samples as well as nylon (70 wt%) and glass fiber (30 wt%) composite. To better understand the effect the kaolins may have on the crystallinity of the nylons, XRD and DSC tests will also be conducted.

The tasks in this study can be summarized as follows:

1) Investigate the effects of kaolin addition on the properties of nylon composites using microscale fabrication. This will be accomplished by the following:

- Produce composites containing PA6 with glass fiber only and with kaolin/glass fiber to compare their mechanical properties.
- Choose the best performing formulations and replace the polymer matrix with compatibilizers to understand the effects on the mechanical properties

- Eliminate glass fibers and understand the effects on the mechanical properties of PA6-mineral only composites
- Choose the best performing kaolins and repeat the analysis by replacing PA6 with PA66 as the polymer base

1.7 Organization Of Thesis

This thesis consists of five chapters:

Chapter (1): A brief introduction into the topic of polymers, kaolin as a filler and thermoplastic composites. It also includes the problem statement and the objectives of this study.

Chapter (2): The materials and methodologies used in the study are presented along with various formulations.

Chapter (3): The results from the analysis of PA6/glass fiber/kaolin composites are discussed first. The best performing formulations are used in a second trial where a compatibilizer is added and the mechanical properties re-examined.

Chapter (4): Results from eliminating the glass fibers are discussed. A second phase is conducted with the best performing minerals and the analysis is repeated in a PA66 polymer matrix base. Additional results regarding the crystallinity of the materials are also discussed to better understand the behavior of the kaolin.

Chapter (5): Conclusions are presented along with recommended future steps.

MATERIALS AND METHODS

1.8 Materials

The primary polymers used in this study are nylon 6 and nylon 66. They were chosen based on prior results [Baioumy] due their preferable mechanical properties. As discussed previously, they are also some of the most widely used polymers in industry with various applications in fields such as automotive and marine. The nylon was first dried and kept in a sealed LDPE bag until it was used as it is a hygroscopic resin and can contain up to 2.5 wt% of water at room temperature. Details on the drying process are provided below. The nylon 6 used in this study is B-27E obtained from BASF (BASF Ultramid B3L) and the nylon 66 is DuPont Zytel ST801. The data sheets for the respective polymers are attached in Appendix A.

The reinforcement for the composites was glass fiber. The fibers were obtained from Owens Corning and were of the grade ME1510 [Owens Corning]. They were chopped in the lab to a length of 1" ± 1/8".

Imerys provided the Kaolin minerals which are classified according to the production year, kaolin family, surface treatment and processing conditions. Due to the proprietary information regarding the exact composition of the minerals, a generic naming scheme was given to the minerals. The kaolin minerals used in this study along with their properties such as surface treatment, particle size and aspect ratio are shown in Table 4. These properties will be used to better understand the effects of the kaolin on the properties of the composite. Throughout the study, different ratio of the polymer, kaolin and glass fibers are used and are stated as such in each section.

The compatibilizer used in this study was Dow AMPLIFY™ GR 216 and is a commonly used functional polymer [Dow]. The amount of the compatibilizer used was between 0 and 5 wt%. These values were chosen in accordance with the data sheet provided by Dow and were used to establish an optimum amount of compatibilizer to be used in the composites that can improve the dispersion of the kaolins within the polymer without compromising the impact strength.

Table 4 List of Kaolin minerals used and their major differences

Mineral	Treatment	Particle Size	Aspect Ratio
Hydrite SB60	Untreated	Fine	Large
Hydrite UF90	Untreated	Very Fine	Negligible
Glomax LL	Calcined treated	Large	Negligible
Polarite 102A	Calcined treated	Large	Negligible
Polarite 402A	Calcined treated	Fine	Negligible
Translink	-	-	-
XP15-0006	Surface treated	Fine	Large
XP15-0600	Surface treated	Medium	Large
XP15-0621	Surface treated, different to XP15-0600	Medium	Large
XP15-0700	Surface treated	Fine	Medium
XP15-0800	Calcined treated	Large	Negligible
XP15-4100	Untreated	Large	Large
XP15-4190	Untreated	Very Fine	Negligible

1.9 Fabrication Techniques

To remove any entrapped moisture from the nylon 6, a drying protocol was followed. The drying temperature was set to 80°C and the pellets were left to dry for 3 ± 0.25 hours according to thermogravimetric analysis that determined the necessary temperature profile (temperature vs time) necessary to dry the nylon as reported in [Baioumy]. Similarly, the nylon 66 was dried for 5 ± 0.25 hours, as specified by the polymer manufacturer. The nylons were then immediately transferred to LDPE bags to prevent any moisture absorption and were cooled for approximated 24 hours before fabrication of the composites.

In order to compare the kaolin fillers relative to each other, multiple sets of composites with different kaolin minerals and glass fiber contents were fabricated in the shape of dogbone and flex bars. Melt compounding and injection molding were used to produce the samples. The specimens were fabricated using tabletop micro extruder connected with a transfer mold with a micro injection-molding unit. These are shown in Figure 1.

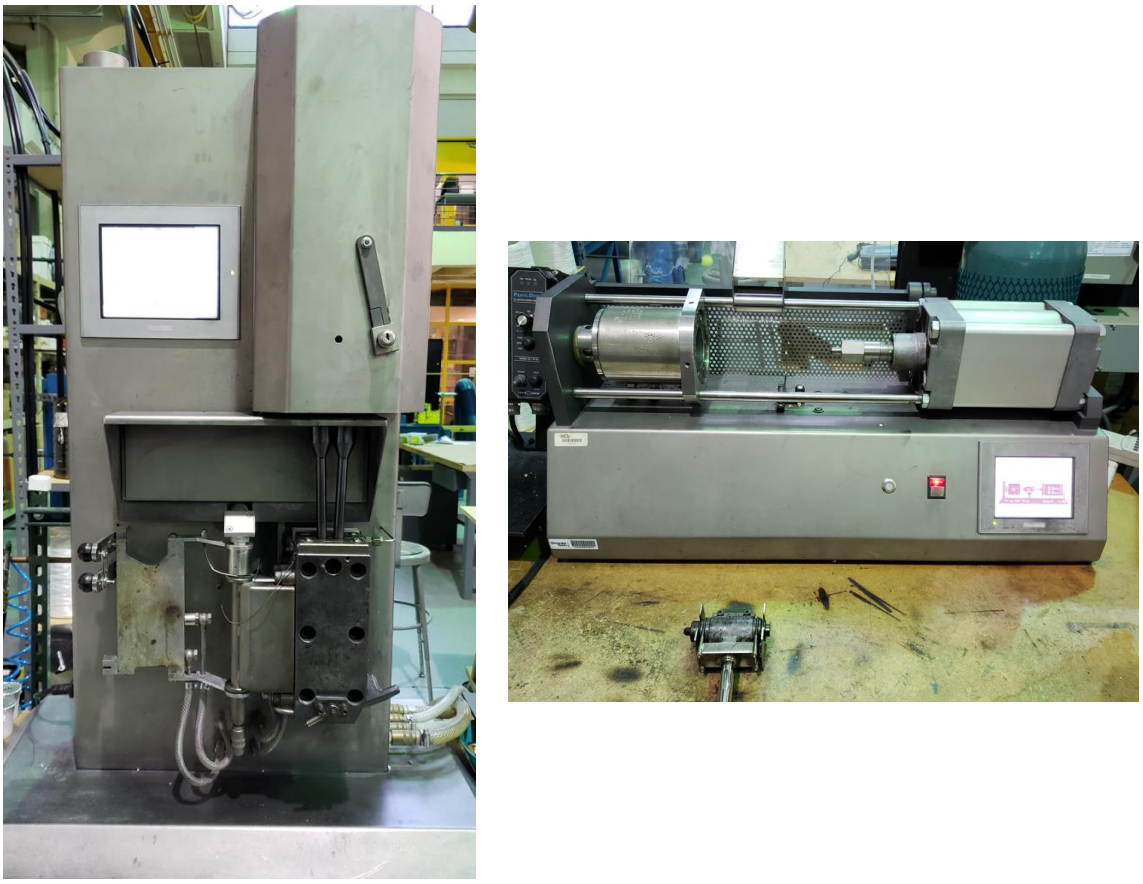

Figure 7 Twin-screw micro extruder and injection molding machine

To prepare the material for feeding into the compounder, batches of 10g were weighed in lab cups in the relative proportions of nylon, mineral and glass fibers with no premixing done beforehand. The material was then fed into the hopper and fed in a manner such that the kaolin was fed first with the nylon pellets following. This was done in order to prevent accumulation of the minerals at the top of the barrel. The process parameters are mixing time of 3 minutes. During this time the materials in the compounder barrel are mixed and the polymer pellets melt. Then the melt is transfered into the micro injection-molding machine using the transfer gun and is injected into the mold to create the parts. The temperature in the barrel, in the transfer gun and in the mold as well as the speed of

the screws in the barrel and the pressure profile during injection molding are the other process parameters that were optimized for the specific material system.. The set values for these process parameters are detailed in Table 5. In between formulations, the compounder barrel was purged with nylon 6/nylon 66 (depending on the formulation) to clean out any residue and contamination. A dummy specimen was also made before each new formulation and discarded in order to ensure that the gun and the mold were cleansed of any residue. The samples produced are shown in Figure 8 and follow the ASTM guidelines for flex and tensile samples (63.5x12.8x3.2 mm for flex and Type V bars for tensile). Once all samples were produced, Asaclean purging compound was used to clean the barrel and the gun. Stainless steel brushes were then used to rid the equipment of any residue.

Table 5 Compounder settings for nylon 6 and nylon 66 formulations

	Nylon 6	Nylon 66
Barrel Temperature	250 °C	290 °C
Melt Temperature	230 °C	260 °C
Gun Temperature	240 °C	290 °C
Mold Temperature	80 °C	80 °C
Mixing time	3 minutes	3 minutes

Injection pressure	8 bar for 5 seconds	8 bar for 5 seconds
Filling pressure	12 bar for 10 seconds	12 bar for 10 seconds

Figure 8 Flex and tensile samples

The following set of composite specimens were made:

i) Nylon 6 composites containing 15 wt% GF and 15% kaolin (various kaolins were used)

ii) Nylon 6 with 30 wt% GF composites which were used as control/baseline.

iii) Nylon 6 composites containing 15 wt% GF and 15 wt% XP15-0600 kaolin with compatibilizer amount varying from 0 to 5 wt% at a step of 1 wt%, in order to understand the effect of compatibilizer

iv) Nylon 6 composites containing only 30 wt% kaolins in order to explore the potential of kaolins to replace GF

v) Nylon 66 composites containing 30 wt% kaolins, those that resulted in nylon 6 composites with the best performance.

1.10 Characterization Techniques

The tests shown in Table 6 detail the procedures followed to obtain the corresponding properties for the composites. SEM, XRD and DSC were also performed to gather additional information.

SEM imaging was performed using Zeiss Ultra with varying degrees of magnification to better understand the surface morphology of the kaolin fillers as well as the failure mechanisms of the composite samples. The SEM images were taken on the fracture surfaces of the used tensile and impact samples. No further processing was done on the samples. XRD tests were run using PANalytical Alpha-1 MPD instrument, in order to determine any potential effects of the kaolins on the crystallinity of the nylons. DSC tests were run using TA DSC Q2000 and helped to further understand the crystallization behavior of the kaolin samples. The temperature ramp rate was controlled at 10°C/min and the material was heated from 30°C up to 250°C for nylon 6 and 320°C for nylon 66 and held at that temperature for 5 minutes before cooling back down to 30°C. A single run was performed for various samples, as stated in the following chapters.

Table 6 Testing methods and standards

Test	Testing standard	Properties Obtained
Tensile	ASTM D638	Tensile Strength, Tensile Modulus, Strain at break
3-point bend	ASTM D7264 /790	Flex Strength, Flex Modulus
Izod Impact	ASTM D256	Impact Strength/ Unit Area
Izod Notched Impact	ASTM D256	Notched Impact Strength

The mechanical properties of the composites with the formulations mentioned above produced using the twin screw compounder with nylon 6 as the primary base polymer are presented in the next chapter.

INCORPORATING KAOLINS INTO GLASS FIBER-NYLON 6 COMPOSITES

1.11 Introduction

This chapter presents the properties of nylon 6 composites containing glass fibers and kaolin to help better understand the synergies between the constituents and the possible substitution of glass fibers with kaolin. The reason for doing so is two-fold. Glass fibers currently used in industry lead to excessive tool wear due to their abrasive nature. By substituting the use of glass fibers with kaolin, tool wear can potentially be decreased leading to an increased tool life and eventually lower productions costs. Secondly, kaolins can potentially provide a much better surface finish to composite components. This is due to their smaller size which allows smoother surfaces even if the kaolins are not homogeneously dispersed within the polymer. Hence, for applications requiring higher aesthetic finishes, this application can be very useful.

The samples were produced according to the method presented in chapter 2 and were tested against the properties listed in Table 6, which include tensile strength and modulus, flexural strength and modulus, and notched and unnotched impact strength.

1.12 Mechanical Properties

Figure 9 - 11 show the tensile, flexural and impact properties respectively of the various formulations produced in a nylon 6 polymer matrix. All samples contain 70 wt % nylon 6 and were produced with 15 wt % of glass fibers and 15 wt % of kaolin, except for “GF Only”, which was produced with 30 wt% glass fibers and no kaolin. The error bars

displayed in the figures show +/- 1 standard deviation from the mean of 7 to 8 samples. The “GF Only” formulation is treated as the control group and benchmark.

In terms of tensile strength, the control samples containing only glass fibers in a nylon 6 base performed the best. This was expected since the high glass fiber content allows for better loading and stress transfer between the matrix and the fibers. Furthermore, the glass fibers were 1-inch-long (although their length may have been further reduced within the extruder due to the shear stresses present and the friction between the material and the rotating screws) and are able to better carry stress. According to the discontinuous fiber model presented in Mallick, the shear stresses originate at the ends of the fibers and build along the length of the fiber until the maximum load carrying capacity is reached. The enhancement of the strength indicates that the fibers length is larger than the critical length required for the fibers to be fully loaded and carry load equal to their strength.

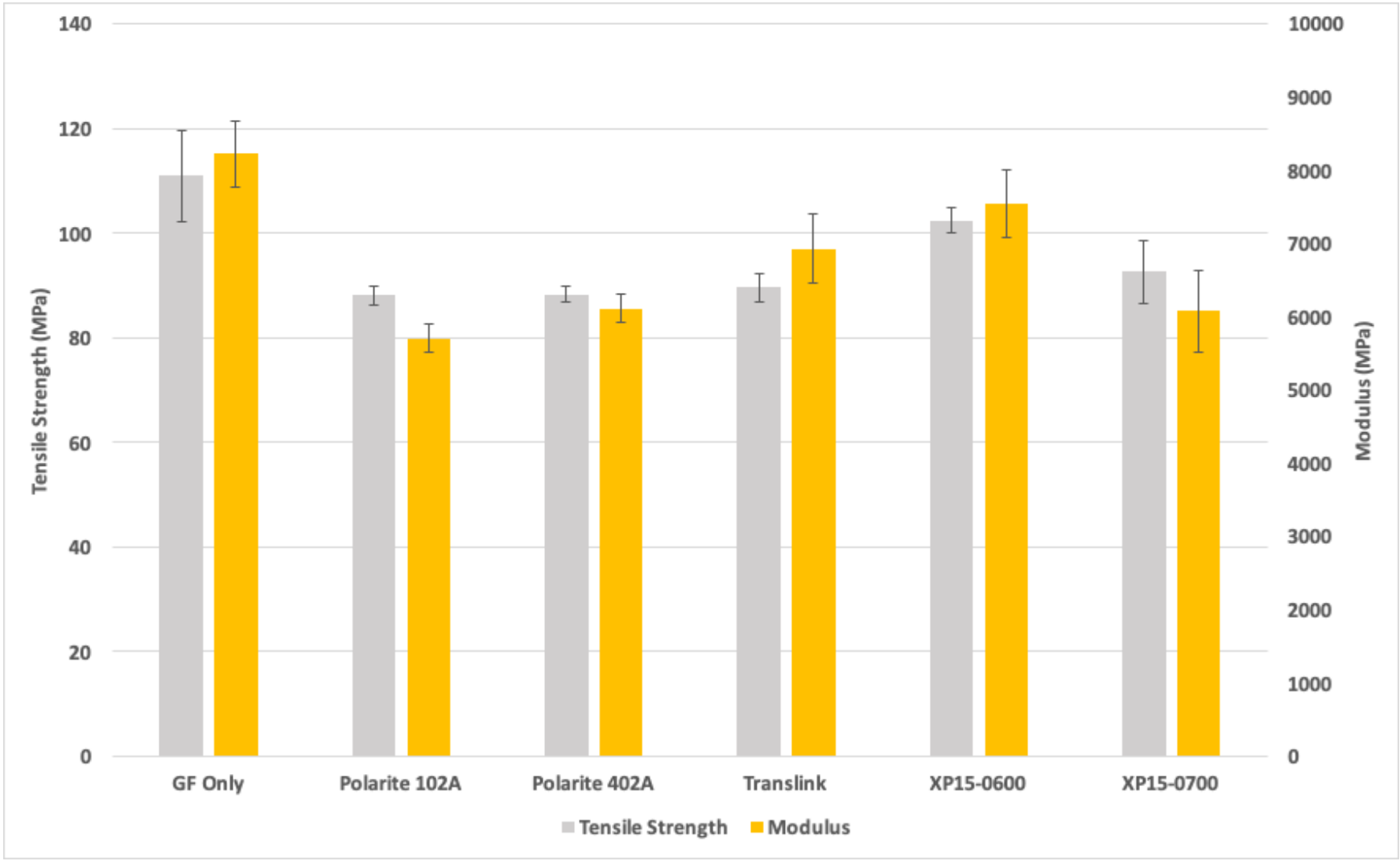

Figure 9 Effect of kaolin type on the tensile properties of GF-Nylon 6 composites containing 15 wt% of GF and 15 wt% of kaolin. The "GF Only" formulation contains 30 wt% of GF and no kaolin

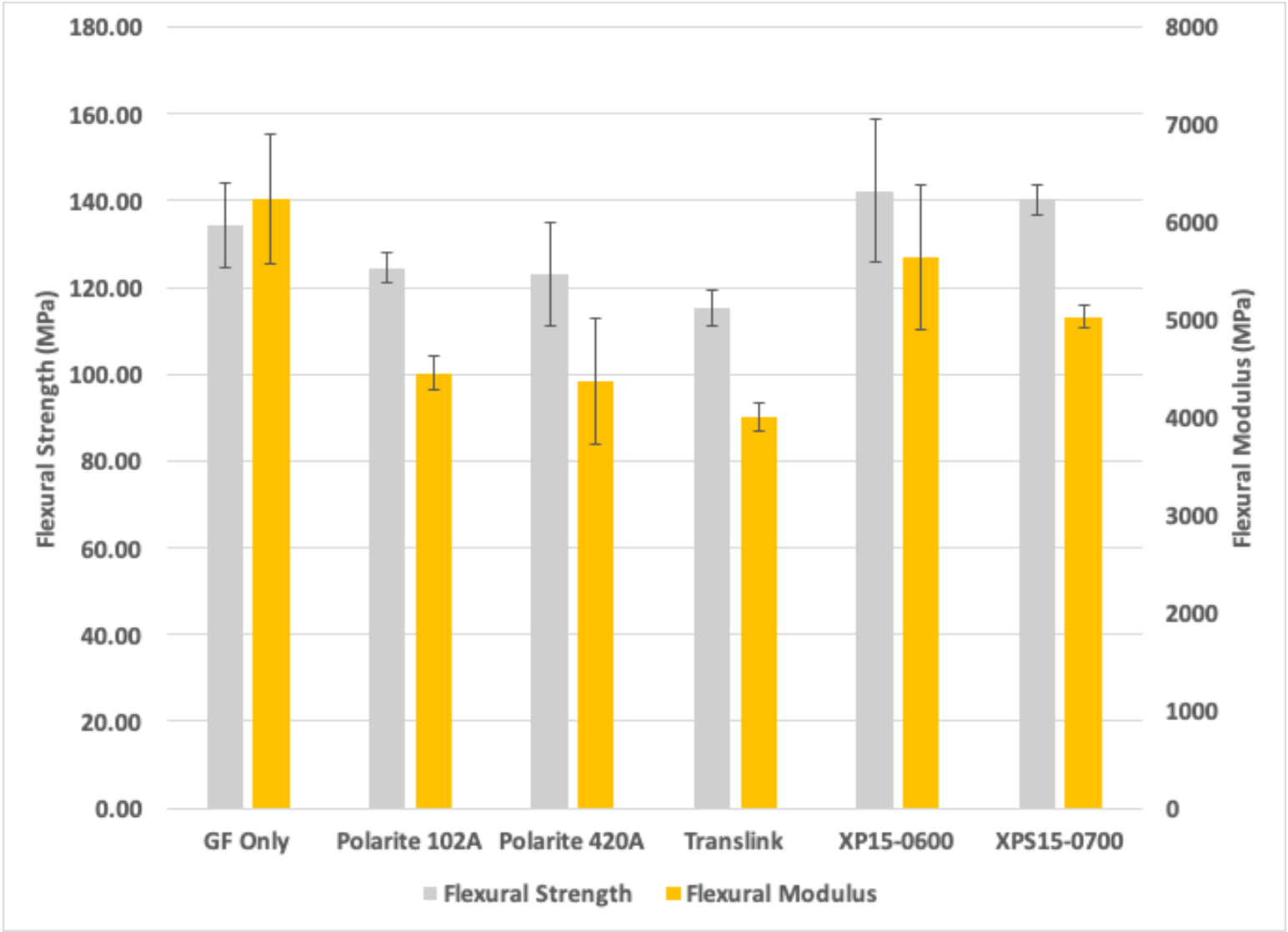

Figure 10 Effect of kaolin type on the flexural properties of GF-Nylon 6 composites containing 15 wt% of GF and 15 wt% of kaolin. The "GF Only" formulation contains 30 wt% of GF and no kaolin

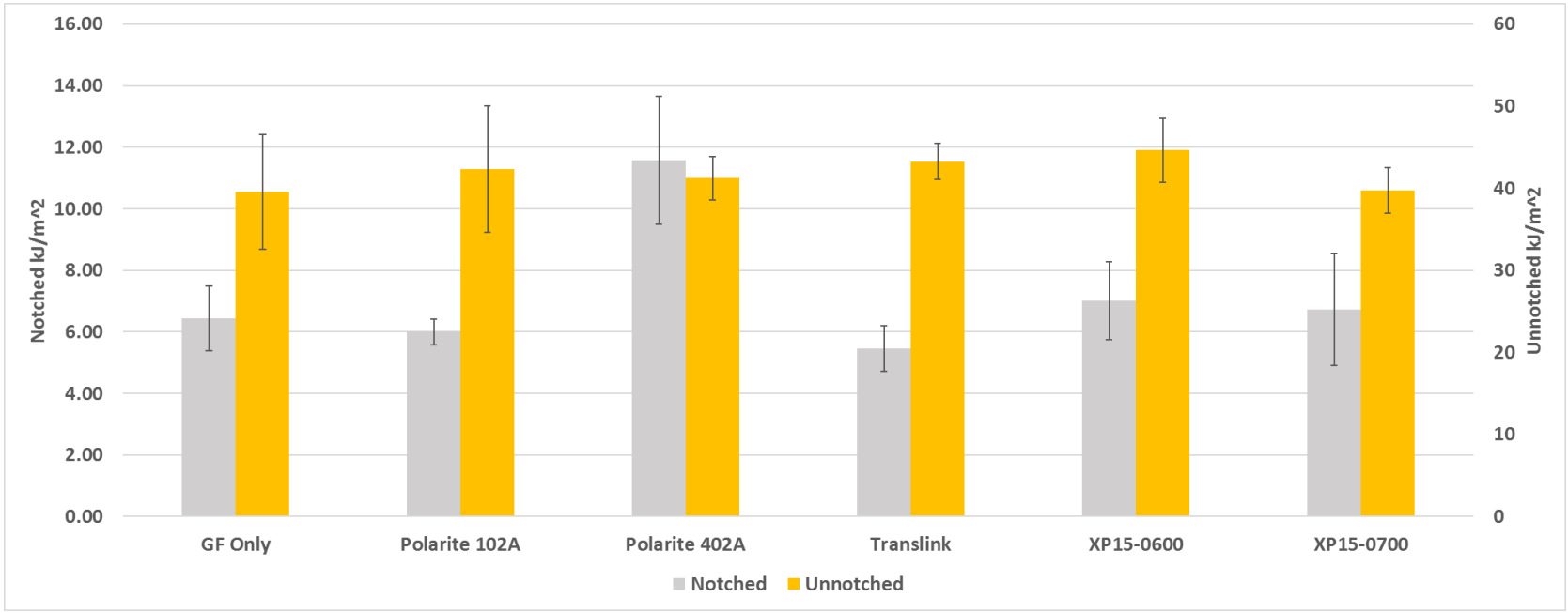

Figure 11 Effect of kaolin type on the impact properties of GF-Nylon 6 composites containing 15 wt% of GF and 15 wt% of kaolin. The "GF Only" formulation contains 30 wt% of GF and no kaolin

The best performing formulation containing kaolin was XP15-0600 (15wt% GF/15wt% XP15-0600). Its tensile strength came within 10% of the control sample (GF only). The tensile modulus was also the highest amongst other kaolin-GF formulations with a mean value of 7.5 GPa, which is close but still lower than the mean value of 8.3GPa of the control sample. It also had the highest flexural properties amongst the other kaolin samples and the second highest mean impact strength. However, it falls short in performance as compared to the GF only samples containing 30 wt% GF.

The XP15-0600 is a surface treated medium sized clay with a large aspect ratio. As discussed by Tandon and Weng [Tandon and Weng], a larger aspect ratio can contribute to an increased elastic modulus. This is due to the fact that the inclusions (kaolin) allow for a more uniform transfer of stresses along the axis of the particle. Some of the assumptions made by Tandon and Weng include the alignment of the particles in a single direction. These assumptions are applicable to this study since the particles can be fairly aligned due to the injection molding machine apply force in a singular direction during the extrusion and injection molding process. This effect also helps to explain why Polarite 102A and Polarite 402A, which have a negligible aspect ratio, perform worse as compared to XP15-0600. Translink 445, a surface treated kaolin produced by BASF and widely used worldwide in nylon 6 composites [Translink] also performed lower than XP15-0600 in both notched and unnotched tests. Translink is a direct competitor to Imerys kaolin products and it can be hypothesized that it has a lower aspect ratio than XP15-0600 due to its inferior performance.

It is also worth noting that the impact strength of the kaolin-GF samples is comparable to that of the GF only samples for both notched and unnotched tests. This can

be explained through a few mechanisms. As discussed by Riley et al. [Riley et al.], the inclusion of fillers can lead to high stress concentration locations within the sample, with higher aspect ratios leading to higher stresses. This compliments the data obtained where Polarite 402A (with an aspect ratio ~1) performs better in impact as compared to XP15-0600 (a higher aspect ratio). He and Jiang [He and Jiang] introduced the percolation theory model which states that a percolation network can be formed between the particles if the matrix zones around each particle are small enough and close to each other. This can lead to an increase in the modulus since the stresses can be distributed more evenly across the percolated network. However, smaller particle sizes tend to lead to agglomeration. Severe agglomeration can lead to multiple sites of stress concentrations and crack-initiation. When comparing 2 fine particle kaolins (Polarite 402A and XP15-0700), it can be noted that both had similar unnotched impact strengths. However, Polarite 402A had a 72% higher notched impact strength. This can be attributed to 2 factors: 1. Polarite 402A particles had a smaller aspect ratio which led to lower stress concentrations as described previously. 2. Polarite 402A particles were calcine treated rather just surface treated. Since not much information is available regarding the surface treatment of the two products due to proprietary information, it can be assumed that the aspect ratio played a greater role in the impact strength increase.

As reported by Baioumy, there is an inverse trend between the particle size of the kaolin mineral and the mechanical strength and modulus. The large particles of Polarite 102A perform worse than the medium and fine particles of XP15-0600 and XP15-0700, respectively. However, this difference cannot be attributed solely to the aspect ratio and size of the particles. Dispersion of the mineral itself in the polymer matrix accounts for a

great degree of the properties produced. The surface area in contact with the matrix tends to have a positive impact on the mechanical properties of the composite. Finer particle sizes lead to larger surface areas and hence a better contact with the matrix. However, the smaller the particle size, the greater is the risk of aggregation, which can unfavorably affect the mechanical properties of the composite such as impact resistance [Leong et al.]. Leong describes the presence of kaolin 'books' which are aggregates held by strong hydrogen bonds between the octahedral hydroxyl face and tetrahedral oxygen face of adjacent particles. It is important to differentiate these aggregates with agglomerates. Agglomerates tend to have much weaker forces as compared to aggregates and do not tend to debond as easily. Hence, aggregates lead to a lower tensile strength by acting as a stress concentrator and allowing easy debonding from the matrix. An example of kaolin books from Leong et al.'s study is shown in Figure 12.

In literature, there are multiple arguments regarding particles sizes. A study done by Verbeek showcased that smaller particle size tends to reduce the tensile strength due to the requirement of more polymer for effective binding. On the contrary, in another study done by Li et al, it was claimed that larger particle sizes tend to cause higher interfacial stresses leading to a zone where damage can initiate quickly. Hence, a smaller particle size was found to increase the tensile properties of the composite. In this study, thus far, the smaller particles produce marginally better tensile properties for the composites. However, the data is within error bars and will need to be re-evaluated in a future chapter. In the study done by Ariffin et al., Li's argument proved to be the stronger of the two arguments.

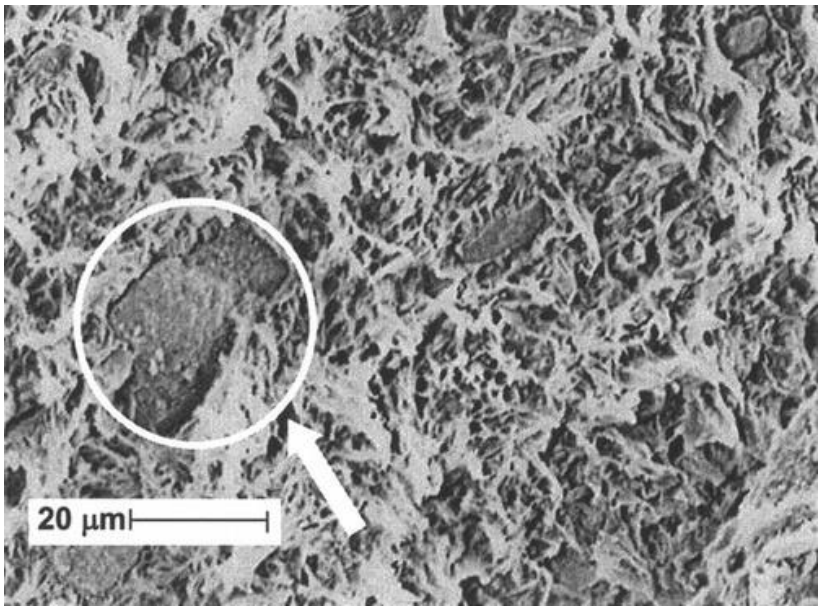

Figure 12 Stacks of kaolin flakes known as books [Li et al.]

When comparing flexural properties, the surface of the specimen and the orientation of the particles also play a big role. Due to the mold and the manufacturing process, the surface of the composite specimen tends to be polymer rich. Due to this fact, when flexural stress is applied on the specimen, it is expected to produce lower values as compared to tensile tests because the bulk of the mineral and glass fibers are concentrated in the interior of the specimen. However, in the experiments conducted during this study, the flexural tests actually produced higher values. This can potentially be explained by two factors involving the manufacturing process. Firstly, it is likely that due to the mixing time of 3 minutes, there was a good dispersion of the minerals and glass fibers in the formulation. This would allow a better distribution of the constituents leading to higher mechanical performance. Secondly, the pressure applied during injection molding might have provided an even flow of the material into the mold, allowing the exterior surface of the specimen to carry higher loads.

Since the amount of GF in the kaolin composites is smaller compared to that in the control GF only composites, it means that there is a lower load carrying ability, especially at the surface of the sample (where stresses are maximum), hence the reduced strength and modulus. Furthermore, the tendency of the kaolin to agglomerate means that the polymer chains have a higher degree of mobility. Thus, the stiffness of the material is expected to be reduced. The only kaolin containing composite that comes close to the baseline specimen is the XP15-0600. It can be hypothesized that the high aspect ratio of the XP15-0600 particles leads to a lower degree of agglomeration which in turn increases the surface interaction between the particles and the matrix. Thus far, the effect of the aspect ratio and particle size can be summarized in Table 7. The converse can also be assumed true for each of the properties specified.

Table 7 Effects of aspect ratio and particle size on mechanical properties

Property	**Direction**	**Tensile**	**Flex**	**Impact**	**Effects**
Aspect Ratio	Higher	Higher	Higher	Lower	Higher stress concentration areas
Size	Larger	Lower	Lower	Higher	Lower risk of agglomeration

1.13 Addition of compatibilizers

After establishing XP15-0600 as the best performing kaolin mineral, this study aimed to focus on improving its mechanical performance by using compatibilizers. The compatibilizer used was Dow AMPLIFY™ GR 216, which is specifically designed to increase the impact strength of nylon composites produced using twin-screw compounding. The GR 216 is a Maleic Anhydride polymer (MAH).

To understand the effects of the compatibilizer, the weight percentage in nylon in the composite was decreased and replaced with an equal weight percentage of the modifier as to keep the total amount of PA6 + compatibilizer at 70 wt%. This was performed for composites containing 0 wt% compatibilizer (control sample) up to 5 wt% compatibilizer, in 1 wt% increments.

1.14 Mechanical Properties With Compatibilizer

Flexural and impact tests were performed on samples containing the compatibilizer. The flexural results are shown in Figure 13 and the impact results are shown in Figure 14.

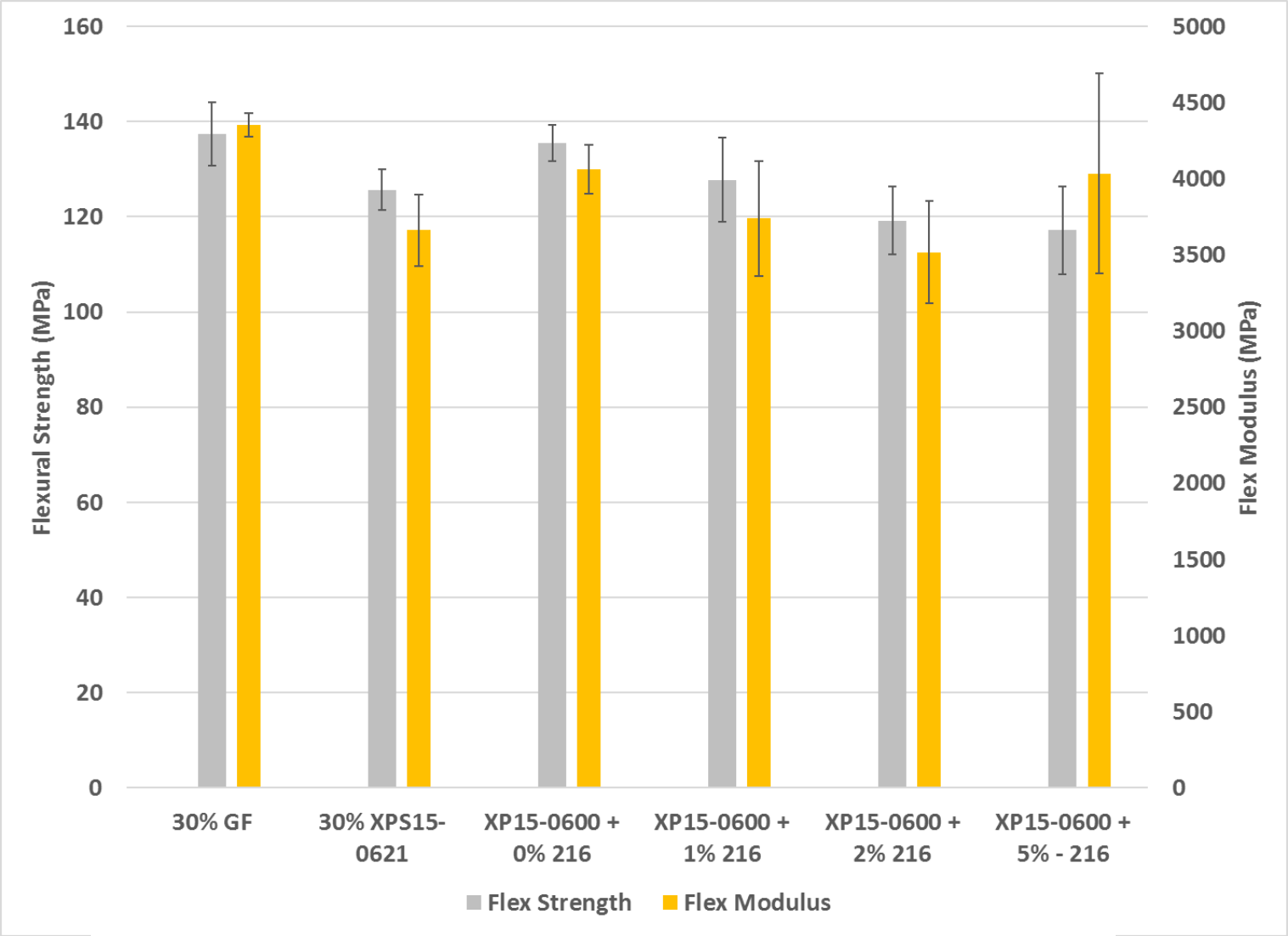

Figure 13 Effect of compatibilizer on the flexural properties of GF-Nylon 6 composites containing 15 wt% of GF and 15 wt% of kaolin. The "30% GF" composite contains no kaolin

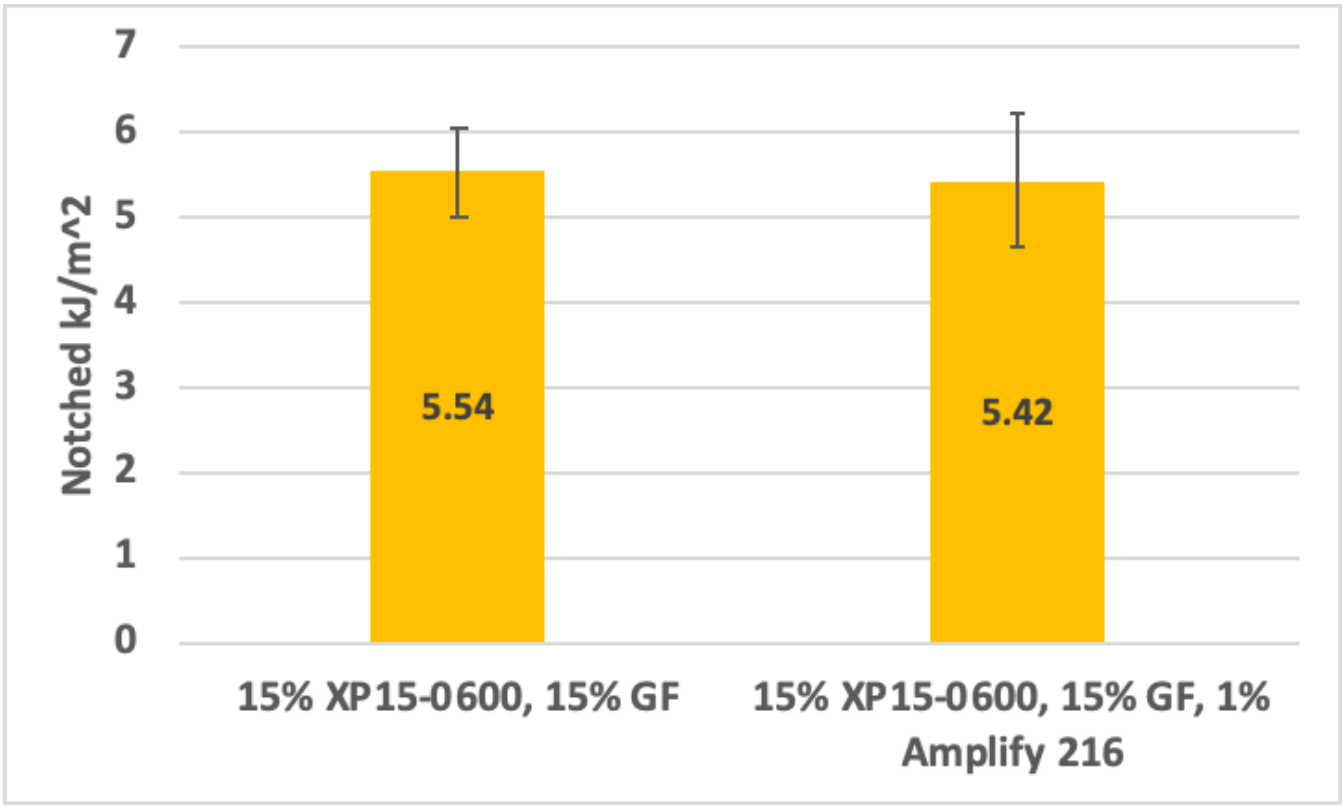

Figure 14 Effect of compatibilizer on the impact properties of GF-Nylon 6 composites

1.14.1 Flexural Properties

Research done by Zeng et al. demonstrated that adding MAH compatibilizers to polymer blends increases the miscibility leading to better dispersion of the polymer matrix. Their study showed that this led to an increased tensile modulus owing to the better dispersion of particles and smaller voids. From the flexural data, a negative trend in the flexural strength and modulus can be observed. This is expected since the compatibilizer is elastomeric in nature and helps increase impact strength at the expense of modulus. By the rule of mixtures, the overall modulus of the composite decreases due to this behavior. According to Arrifin et al, the compatibilizer allows a better interaction between the filler and the polymer matrix. However, beyond a certain point, the MAH leads to more filler agglomerates in the composite leading to a decrease in flexural strength and modulus. The kaolin particles also restrict the movement of the polymer chain thereby further decreasing the deformability of the composite. This mechanism can help explain the decreasing trend seen in the data.

1.14.2 Impact Properties

The impact test did not show a major difference in strength of the composite with 1 wt% of compatibilizer. This may have been due to not having enough compatibilizer to make a significant difference to the chemical structure of the composite. However, it was decided that the decrease in flexural modulus caused by the increase in wt% of the compatibilizer was not worth the trade-off for higher impact strength since in applications pertaining to PA6/kaolin, the flexural modulus is far more important than the impact properties.

1.15 Crystallization Study

To get a better understanding of the crystallization behavior of the composites, a DSC and XRD test was run. Equation 1 was used to measure the degree of crystallinity:

$$\chi\% = \frac{1}{1 - wt\%}\frac{\Delta H_c}{\Delta H_f} \quad (1)$$

where χ is the degree of crystallinity, ΔH_c is the heat of fusion and ΔH_f is the heat of fusion for 100% crystalline and wt% is the weight fraction of the kaolin. The value for ΔH_f was taken to be 185.8 J/g [Inoue] for PA6. The degree of crystallinity obtained for the samples is shown in Table 8.

Table 8 Degree of crystallinity of PA6 composites

Formulation	T_c (°C)	DOC
PA6+XP15-0600	190.99	37.3%
PA6+XP15-0600 + GF	192.48	33.0%
PA6+GF	194.07	37.9%

Pure nylon 6 produces 2 crystalline structures, α and γ. The α phase has monoclinic structure with fully extended nylon 6 chains that forms a sheet like structure. The γ phase forms pleated chains with hydrogen bonds that are perpendicular to the carbon chains [Zhang et al.]. From the XRD diagram of PA6/GF, PA6/GF/XP15-0600 and PA6/XP15-0600, shown in Figure 15, a few noticeable characteristics can be noted. The PA6/XP15-

0600 sample produce multiple high intensity, sharp peaks signaling a highly crystalline structure due to the kaolin particles. On the contrary, the PA6/GF sample produces no distinct peaks and has a small subdued peak around 21°. This relates to an amorphous structure. By combining the glass fibers and the kaolin, a reduction in the peaks produced by the kaolin can be noticed and can be attributed to the loss in the crystalline structure of the kaolin. In a study conducted by Khalil et al, a similar trend was noticed when kaolin particles were dispersed in a PET matrix and the peak intensities provided by the kaolin particles were severely reduced due to the intercalation of kaolin stacks by PEO and KAc, leading to delamination. The right shift of the peaks can be explained due to residual strain in the structure of the kaolin that may have arisen in the sample [Zeng et al.]. The highly crystalline behavior of kaolin can help to explain the strong mechanical performance, both in tensile and flex, exhibited by the XP15-0600 composite. However, it can be concluded that a greater portion of the strength is provided by the glass fibers since the PA6/GF still outperforms the other samples.

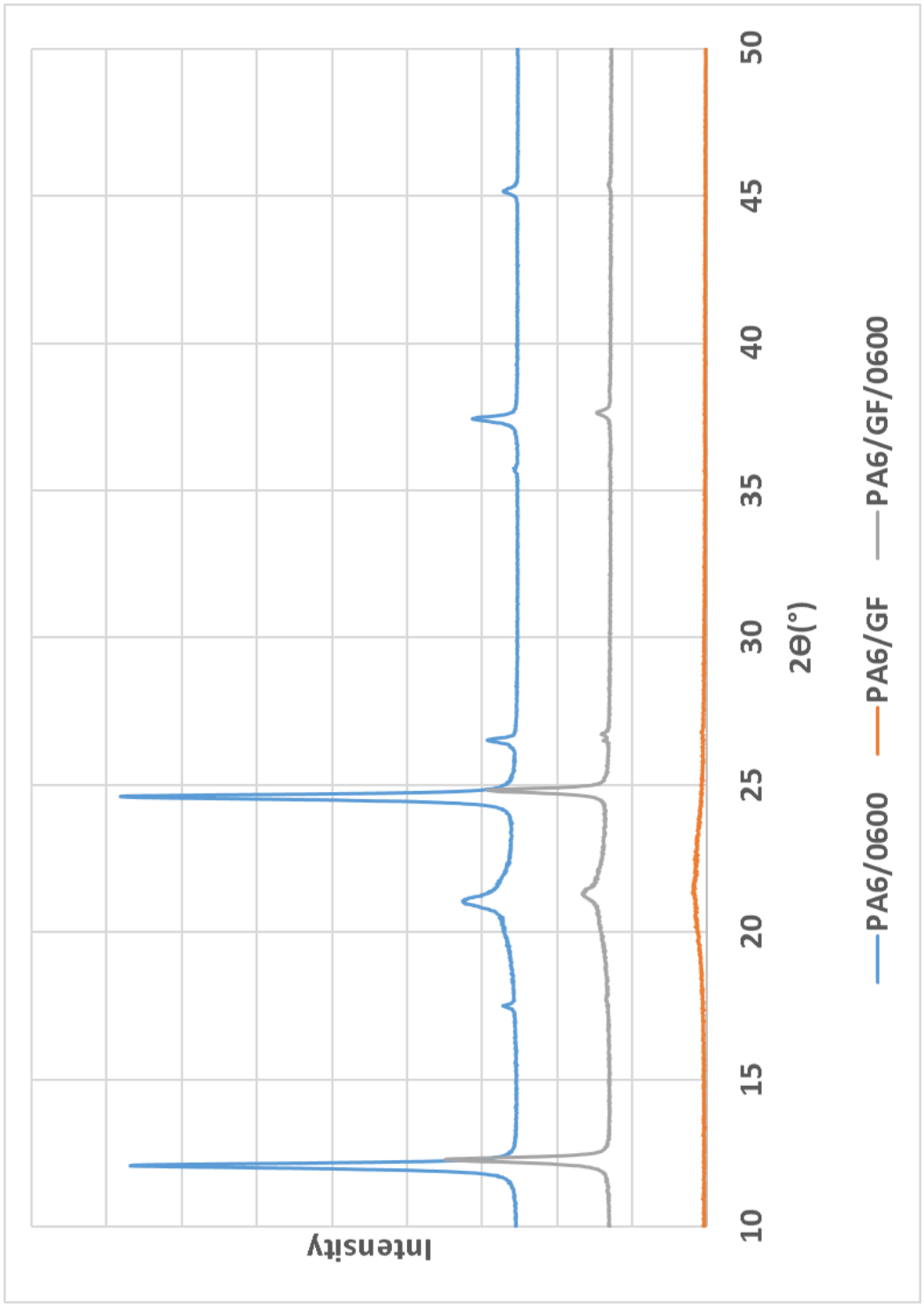

Figure 15 XRD patterns generated by nylon 6 composites

1.16 Surface Morphology Using SEM

SEM imaging was used to investigate the dispersion of the kaolin minerals in the matrix as well as to identify the modes of failure of the composite. As seen in Figure 16, there is considerable matrix debonding and fiber pullouts as the main mechanisms for the fracture. The fiber directions also seem to be fairly disorientated, suggesting a good mixing between the polymer matrix and the fibers. This fact will allow the composite to have an equal load transfer in all directions. However, this could lead to lower values for the flexural and tensile tests since these tests produce the highest values when loading is applied in a singular direction on the reinforcing material. There is also some coating residue evident on the fibers. As discussed by Baioumy, the coating can help lead to a better transfer of stresses at the interface of the fiber and the matrix. This can help to explain why the tensile and flexural properties of the PA6/GF/XP15-0600 composite are close to the values of the PA6/GF samples. Figure 17 shows the fracture surface of the PA6/XP15-0600 composite. The large micro crack is a definitive feature of the fracture along with some agglomeration on the sides. The center, however, is a fairly smooth surface. Figure 18 shows a higher magnification image which helps to see the agglomeration regions in the sample.

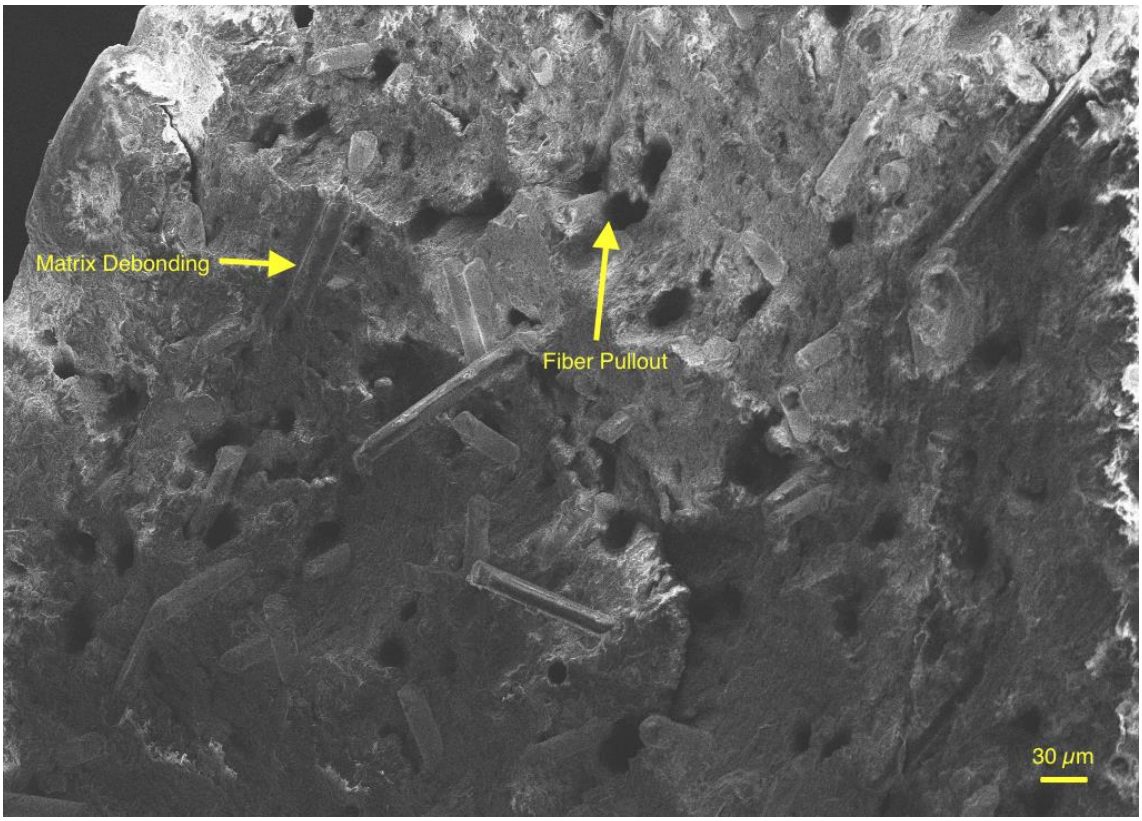

Figure 16 SEM image of fracture surface from edge of impact sample of PA6/GF/XP15-0600 (70wt%/15wt%/15wt%) showing various failure mechanisms such as matrix debonding and fiber pullout

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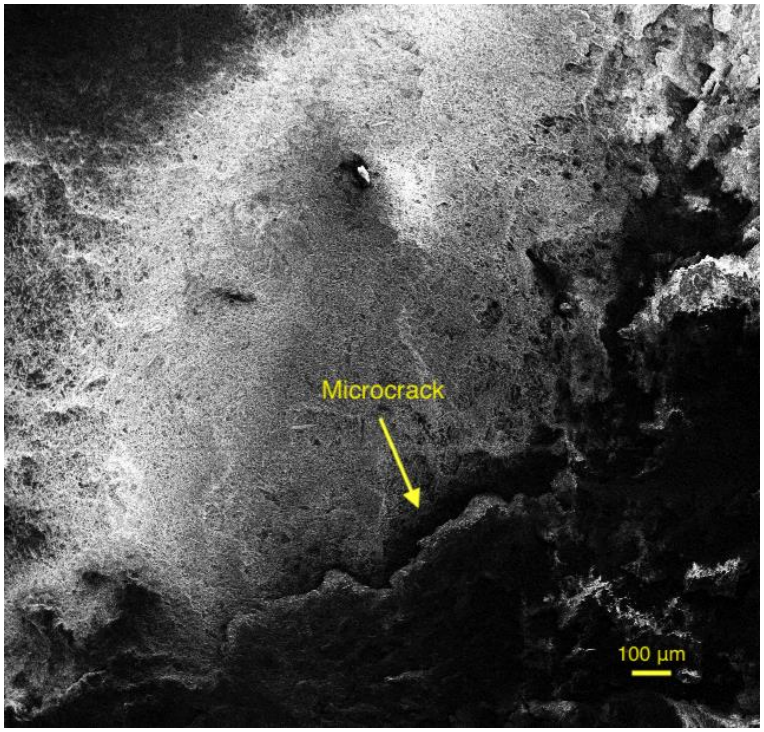

Figure 17 SEM image of middle of impact sample of PA6/XP15-0600 (70wt%/30wt%) showing a microcrack

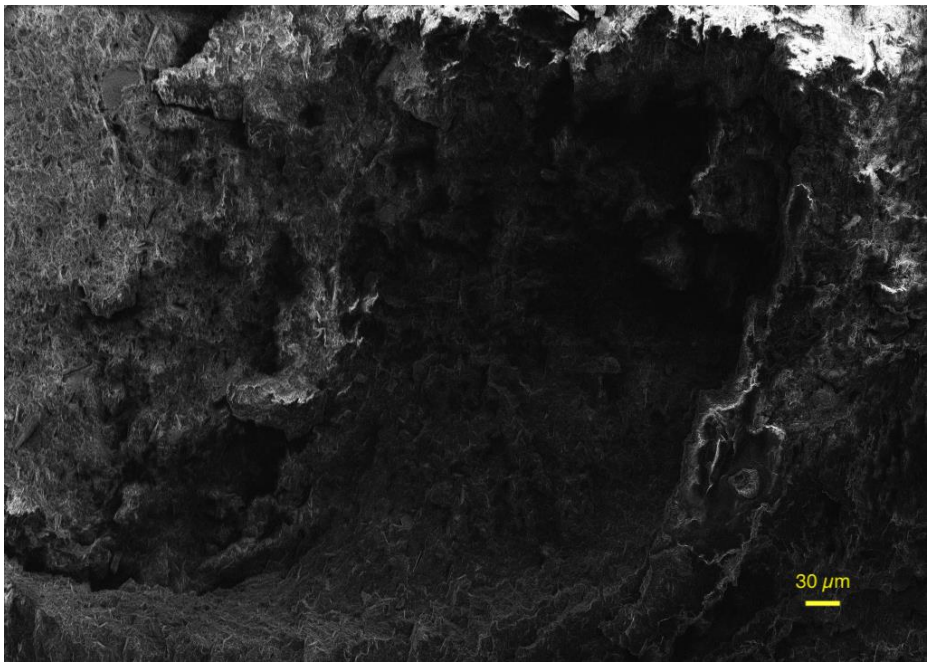

Figure 18 Higher magnification of impact sample of PA6/XP15-0600 (70wt%/30wt%) showing the fracture surface

1.17 Major Findings And Conclusion

In this chapter, the effects of the properties of kaolins such as aspect ratio and particle size were determined and it was established that the strongest performing kaolin in terms of mechanical strength and modulus was the XP15-0600 due to its medium particle size as well as high aspect ratio. The mechanisms for this behavior were reviewed from prior research and examined. The addition of the compatibilizer led to a decrease in the flexural properties of the samples. Due to this reason, the idea of adding compatibilizers to nylon 6/kaolin composites was dropped for the remainder of this study.

As stated in the introduction, kaolins are increasingly being used for automotive applications such as engine and wheel covers. For companies like Imerys, this represents a huge opportunity as a market to enter and expand in. Majority of such applications require high modulus and strength which was noticed in high aspect ratio minerals. Hence, Imerys can further introduce minerals containing higher aspect ratio kaolin platelets to better serve the market.

The following chapter discusses the properties of composites produced without glass fibers. It also evaluates the properties of composites produced with nylon 66 instead of nylon 6 and compares their properties.

ELIMINATING GLASS FIBERS FROM NYLON6/NYLON66 COMPOSITES

1.18 Introduction

Having found the interaction between glass fibers, kaolin and nylon 6, the study now focuses on composites with only kaolin and nylon 6/nylon 66, eliminating the glass fibers. The reason for understanding this new behavior is multi-fold:

1. It allows for a better understanding of the composite without the glass fiber reinforcement, placing a stronger emphasis on the mechanical benefits offered solely by the kaolin
2. It allows for an understanding of the effects the different types of kaolin have on the physical and chemical properties of the composite.

After completing the experiments with nylon 6 as a base, the top 6 performing kaolin minerals were chosen for the second phase of the study along with some new minerals. In the second phase, the polymer matrix was changed to nylon 66. For reasons outlined in chapter 1, nylon 66 can serve as a potential substitute for nylon 6 in thermoplastic applications. Also, the demand for nylon 6 is currently exceeding its supply, allowing nylon 66 to fill a wide gap in the market.

1.19 Mechanical Properties With Nylon 6 Matrix

The mechanical properties of 13 different kaolin formulations were tested for tensile, flexural and impact properties. All formulations contained 70 wt% nylon 6 and 30 wt% kaolin.

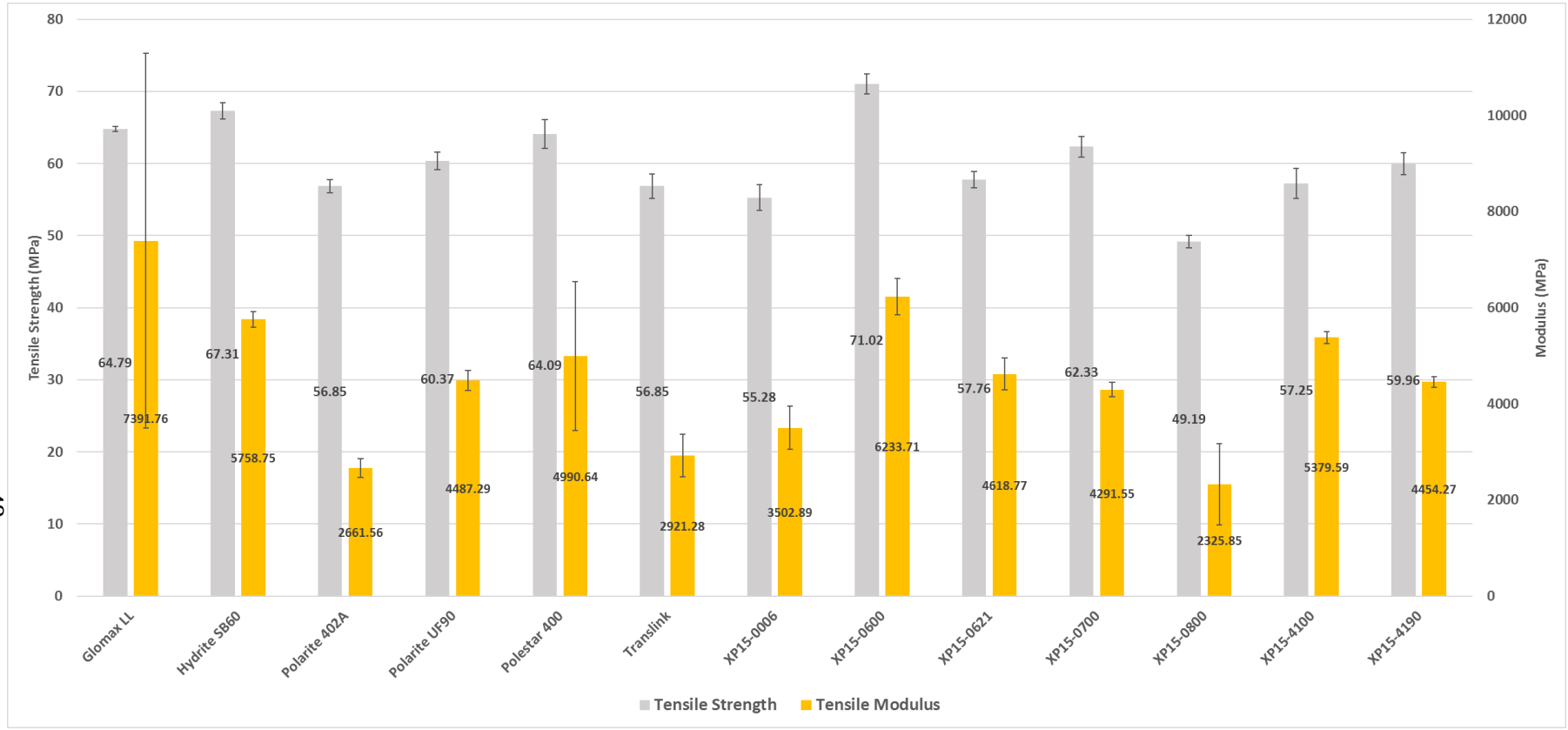

Figure 19 Effect of kaolin type on the tensile properties of nylon 6 composites containing 30 wt% kaolin

1.19.1 Tensile properties

The tensile properties of the samples produced is shown in Figure 19. Similar to chapter 3, the strongest tensile properties were seen in XP15-0600 with a strength of 71 MPa and modulus of 6233 MPa. This can be compared to the values found in chapter 3 where the formulation consisted of 15wt% Kaolin and 15wt% glass fibers and the values for strength and modulus were 102 MPa and 7545 MPa, respectively. The slight decrease in strength and modulus can be attributed to the lack of fibers, which leads to a lesser load carrying ability of the composite and hence a lower strength.

To establish a baseline, the tensile properties of pure PA6 samples were taken from Baioumy's study. The tensile strength and modulus of pure PA6 samples were approximately 70 MPa and 2500 MPa respectively. This indicates a negligible increase in the strength but a 2.5 times increase in the modulus for the XP15-0600 formulation over the pure PA6 sample. It was also discovered that XP15-0621, which has a similar particle size and aspect ratio to XP15-0600, performed worse. The reason for this can be deduced as a difference in the surface treatment of the kaolins. Due to the lack of data on the surface treatments of the kaolins, further analysis due to its effects cannot be performed.

In the previous chapter, the hypothesis presented was that smaller particles tend to lead to higher tensile properties. To test this hypothesis, the values from 3 different minerals can be compared as shown in Table 9. All 3 minerals have similar aspect ratios but differ in the particle size and treatment. The XP15-0600 comes out ahead with the medium particle size, however, this may be attributed to its surface finish. In the untreated minerals, Hydrite SB60 and XP15-4100, it's clear that the finer particle Hydrite SB60

performs 18% better with regards to strength and 7% better with regards to modulus. Hence, it can be concluded that finer particle sizes tend to strengthen the composite more than larger particle sizes. From Li's argument presented in the previous chapter, this can be attributed to the lower interfacial stresses experienced by smaller particles and leading to fewer zones for failure initiation.

Table 9 Comparing the effect of kaolin particle size on tensile properties of nylon 6 composites

Mineral	Surface Treatment	Particle Size	Tensile Strength (MPa)	Tensile Modulus (MPa)
Hydrite SB60	Untreated	Fine	67	5758
XP15-0600	Surface Treated	Medium	71	6233
XP15-4100	Untreated	Large	57	5379

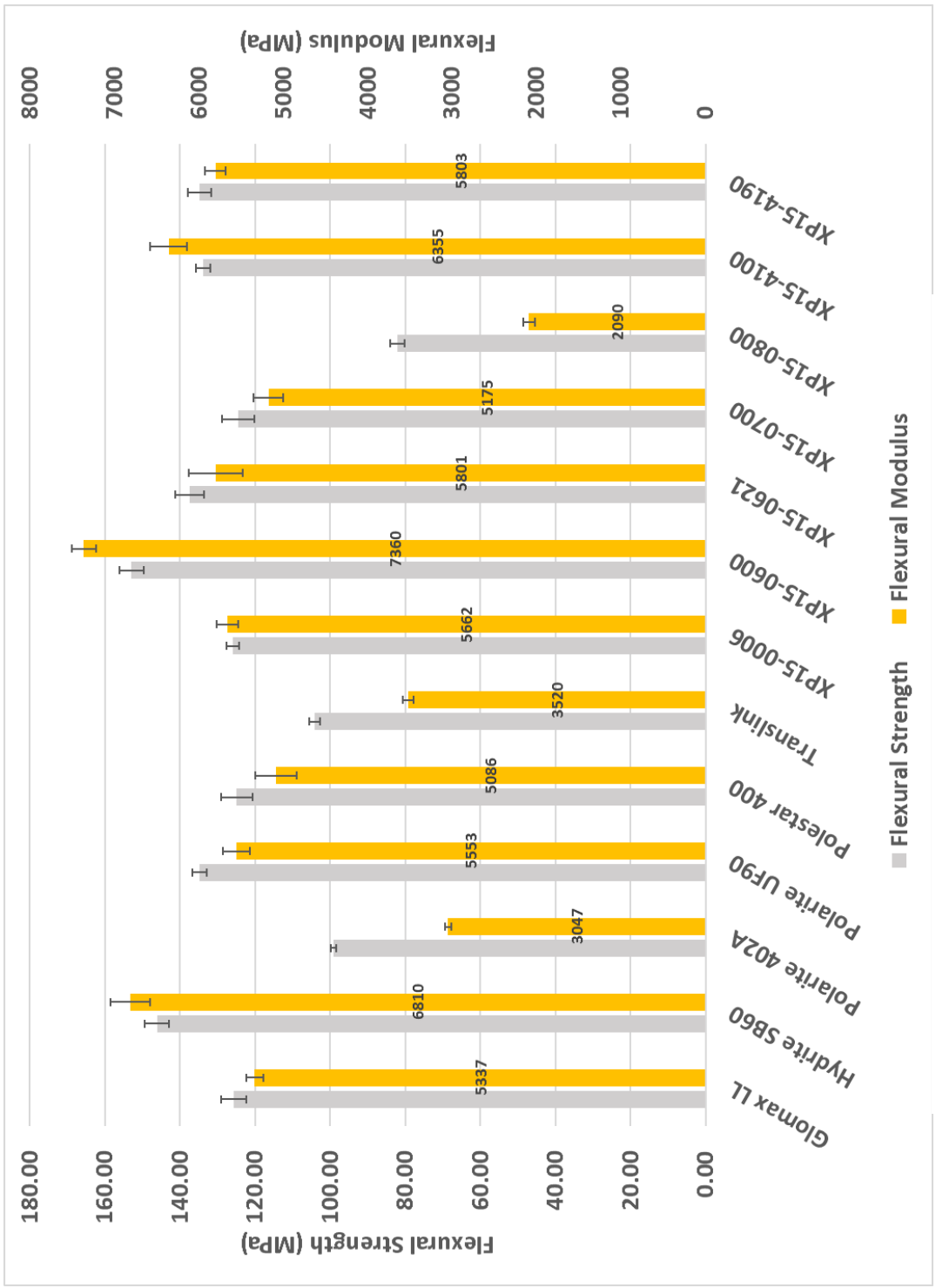

Figure 20 Effect of kaolin type on the flexural properties of nylon 6 composites containing 30 wt% kaolin

1.19.2 Flexural properties

The flexural tests shown in Figure 20 also displayed XP15-0600 as the strongest performer, both in strength and modulus. This is, again, comparable to the values obtained in chapter 3 and suggests that a kaolin with a medium particle size and large aspect ratio is best for applications requiring high flexural and mechanical properties. Comparing these values to those of pure PA6, we get an increase in strength and modulus by 1.8 and 3.7 times respectively, depicting a considerable increase.

The second highest flexural properties were reported by the Hydrite SB60 formulation. The difference in the strength and modulus is 5% and 8% respectively, as compared to the XP15-0600 formulation. However, when comparing to the similar, untreated XP15-4100 with a similar aspect ratio, the trend seen in the tensile properties can be noticed again as shown in Table 10.

Table 10 Effect of kaolin particle size on flexural properties on nylon 6 composites

Mineral	**Surface Treatment**	**Particle Size**	**Flex Strength (MPa)**	**Flex Modulus (MPa)**
Hydrite SB60	Untreated	Fine	146	6810
XP15-4100	Untreated	Large	134	6355

This trend cannot, however, be confirmed with the calcine treated minerals. The calcine treated mineral all exhibit an aspect ratio of ~1 but their flexural strength and modulus vary. Glomax LL, which contains larger sized particles, performs the best and

outperforms many of the finer sized minerals such as Polarite 402A. On the contrary, another large sized mineral, the XP15-0800, has the worst performance out of all minerals. This suggests that particle size alone may not be the biggest contributor to mechanical properties, especially in the presence of other factors such as surface treatment.

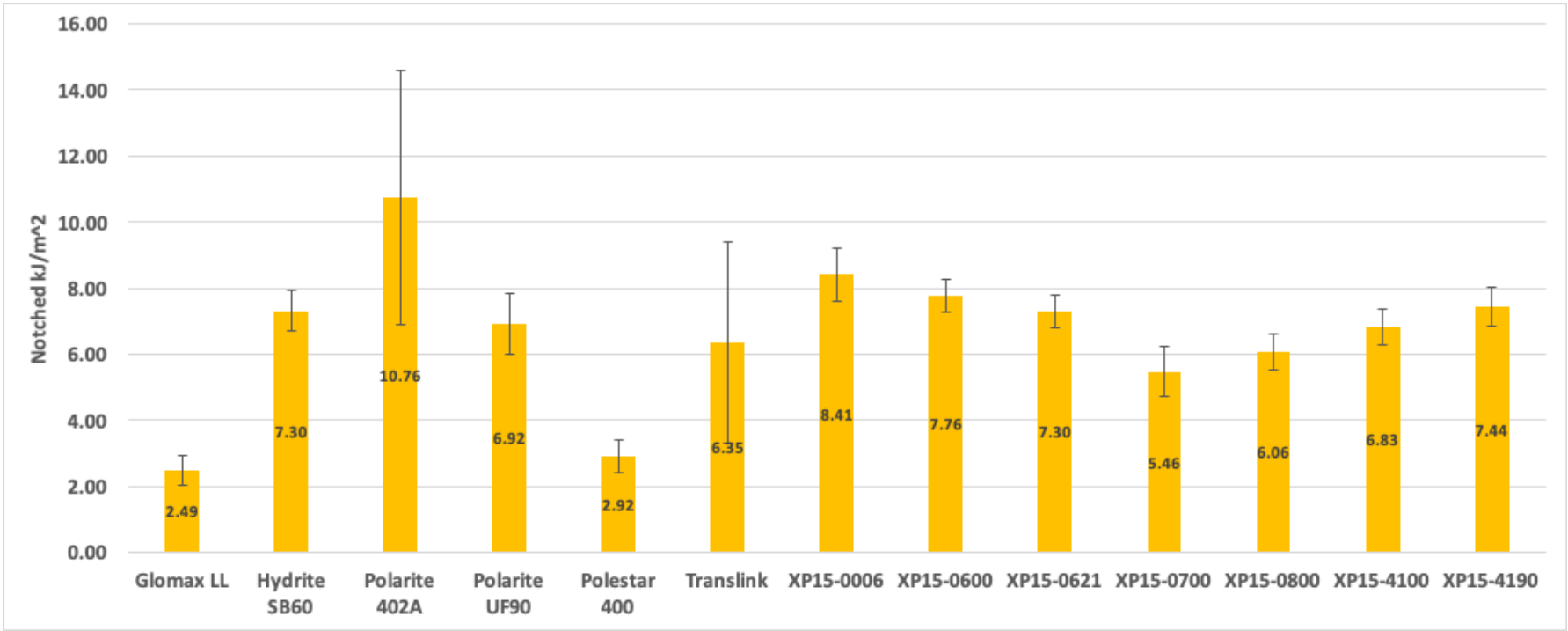

Figure 21 Effect of kaolin type on the impact properties of nylon 6 composites containing 30 wt% kaolin

1.19.3 Impact properties

The data from the impact test can be seen in Figure 21. Polarite 402A performed well in this test, which can be attributed to its small size and negligible aspect ratio. This allows for the kaolin to disperse well in the polymer matrix and absorb more energy [Baioumy]. However, it is important to note that there is a great degree of variability in the values leading to a very high standard deviation. XP15-0006 and XP15-0600 also performed well and came within 28% and 38%, respectively, of the Polarite 402A value.

Based on the mechanical tests performed thus far, it was concluded that the best kaolins were the ones determined and shown in Table 11. To further investigate the interactions of kaolin with polymers, the base matrix was changed from nylon 6 to nylon 66. The mechanical tests performed in the previous sections were repeated and the following results were obtained.

Table 11 Best performing kaolin minerals in nylon 6 composites

Hydrite SB60	XP15-0600
Polarite 402A	XP15-0800
XP15-0006	XP15-4100

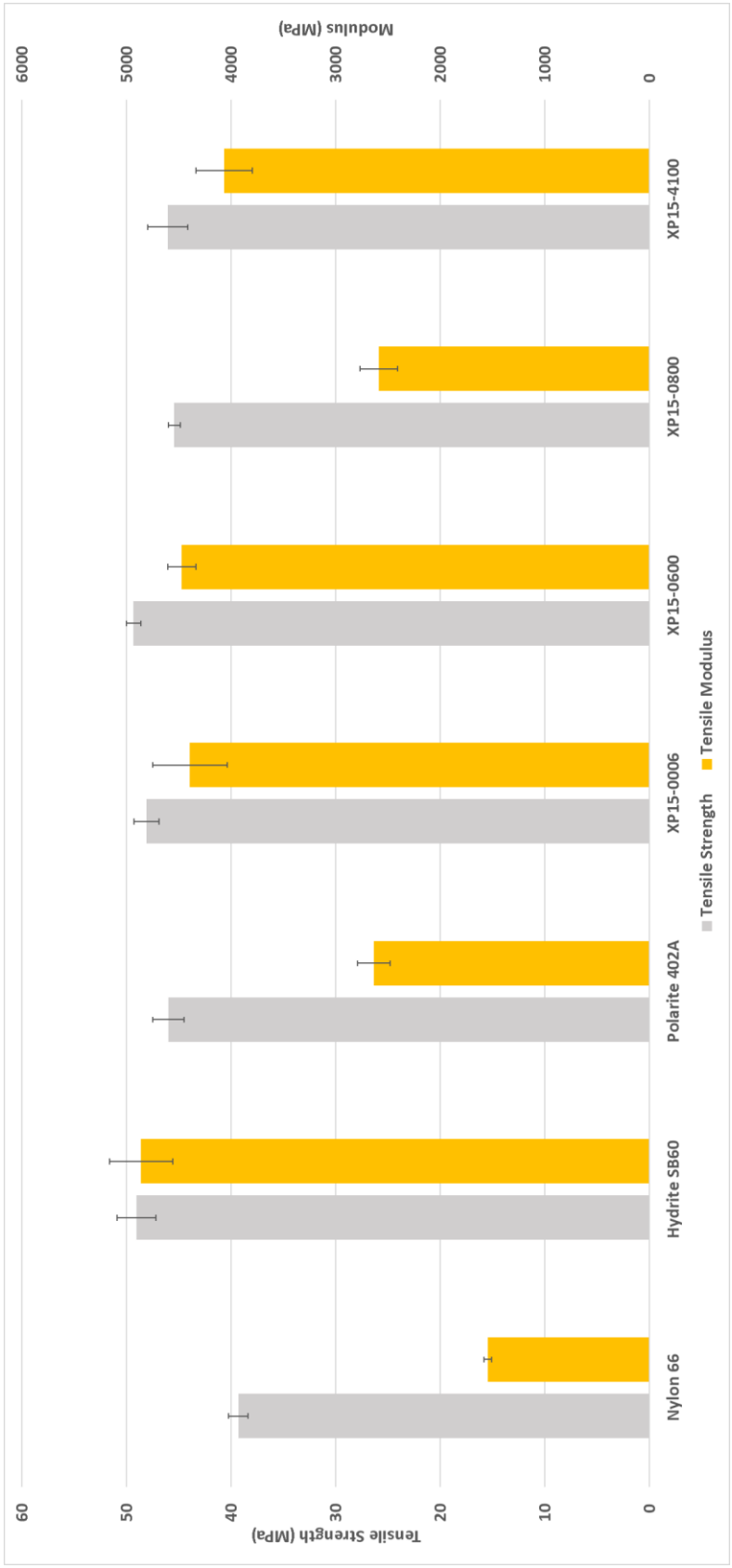

Figure 22 Effect of kaolin type on the tensile properties of nylon 66 composites containing 30 wt% kaolin

1.20 Mechanical Properties With Nylon 66 Matrix

As stated in the previous section, formulations for the 6 best performing minerals were made. Pure nylon 66 samples were also prepared to establish a benchmark for the other formulations.

1.20.1 Tensile properties

The pure PA66 samples had a tensile strength of 39 MPa and a tensile modulus of 1543 MPa. Compared to Baioumy's pure PA6 samples (70Mpa for strength and 2500 MPa for modulus), this value is considerably lower. Although it is expected for PA66 to be a stronger material than PA6 [Ai Engineering Plastics and Laminates], in this case it is not so due to the inherent materials produced by the manufacturers. From the data sheets provided by BASF and DuPont, it was established that the BASF PA6 had higher tensile and flexural properties than the DuPont PA66.

The specimen produced contained 70 wt% PA66 and 30 wt% kaolin in all cases. In the best case with Hydrite SB60, the tensile strength was improved by 25% and the tensile modulus was improved by 214%, which is significant. The improvement seen in PA6 was negligible for the tensile strength and 150% for the modulus. Hence, it can be hypothesized that the nylon 66 shows better synergy with the kaolin minerals, leading to a much a greater improvement in the mechanical performance.

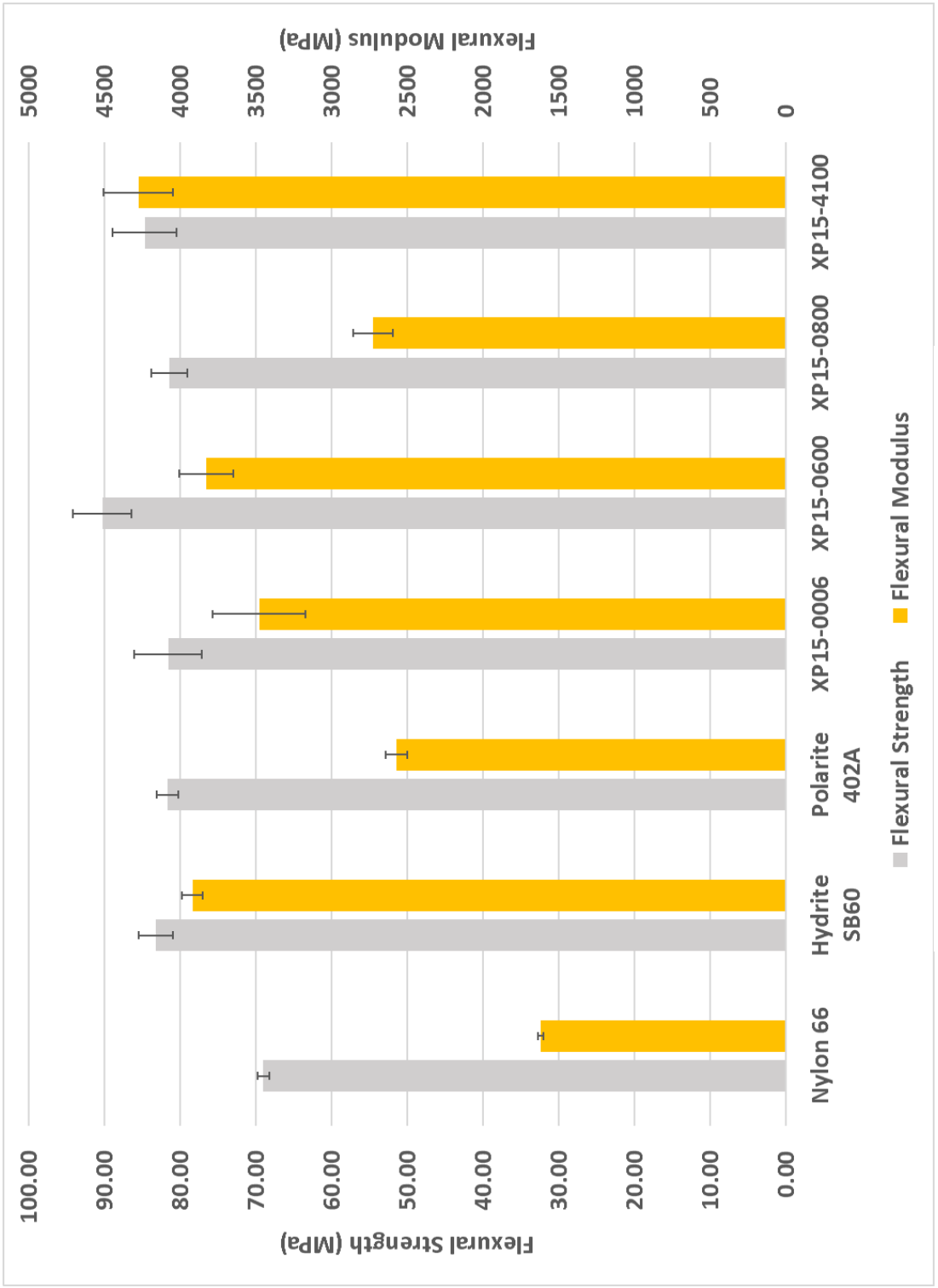

Figure 23 Effect of kaolin type on the flexural properties of nylon 66 composites containing 30 wt% kaolin

1.20.2 Flexural properties

For the flexural properties, the PA66 only sample had a strength of 69 MPa and modulus of 1618 MPa as compared to the PA6 which had a strength of ~80 MPa and modulus of ~2000 MPa. Similar to the tensile case, all the kaolins added to the composite produced higher strength and modulus. The strongest strength was showcased by XP15-0600 which displayed a 31% improvement over the benchmark PA66. The highest modulus was displayed by XP15-4100 which showed a 164% improvement over the baseline. In the PA6/kaolin samples, the greatest improvement seen was 90% in strength and 240% in modulus when compared to pure PA6 samples. Hence, unlike in the case of tensile properties, the flexural properties do not show as much of an advantage when PA66 is used as a polymer matrix instead of PA6.

1.20.3 Impact Properties

The pure PA66 samples did not break under the impact test as they exceeded the test frame's capacity. This is displayed as a missing bar in Figure 24. Similar to the case of PA6/glass fibers/kaolin and PA6/kaolin, Polarite 402A was the best performing kaolin with XP15-0600 coming in second. It is interesting to note that the notched impact values are higher in the nylon 66 matrix than in the nylon 6 matrix.

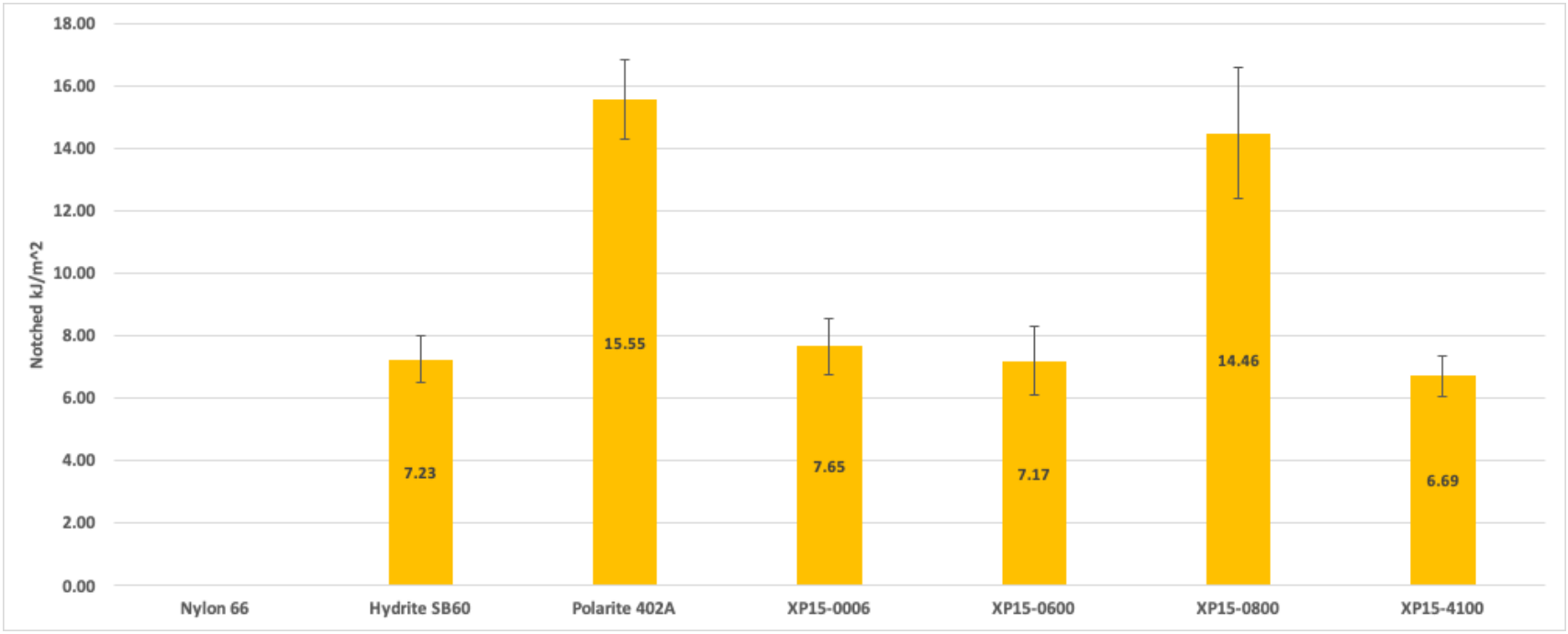

Figure 24 Effect of kaolin type on the impact properties of nylon 66 composites containing 30 wt% kaolin

1.21 Effect Of Kaolins On The Crystallization Behavior Of Nylon

The melting and crystallization for the composites was observed and the results are displayed in Table 12. The value for ΔH_f was taken to be 226 J/g for PA66 [TA]. The increase in the crystallization temperature of the PA66/0600 sample by ~4°C indicates that the 0600 mineral plays a nucleation role in the crystallization of the PA66 matrix [Zhong et al.].

The XRD shown in Figure 25 indicates similar results to the one shown with the PA6 matrix. The kaolin samples produce sharp, intense peaks which are absent in the pure PA66 sample and indicates a highly crystalline system.

Table 12 Degree of crystallinity of PA66 composites

Formulation	T_c (°C)	DOC
PA66	229.21	26.0%
PA66+XP15-0600	233.41	19.1%

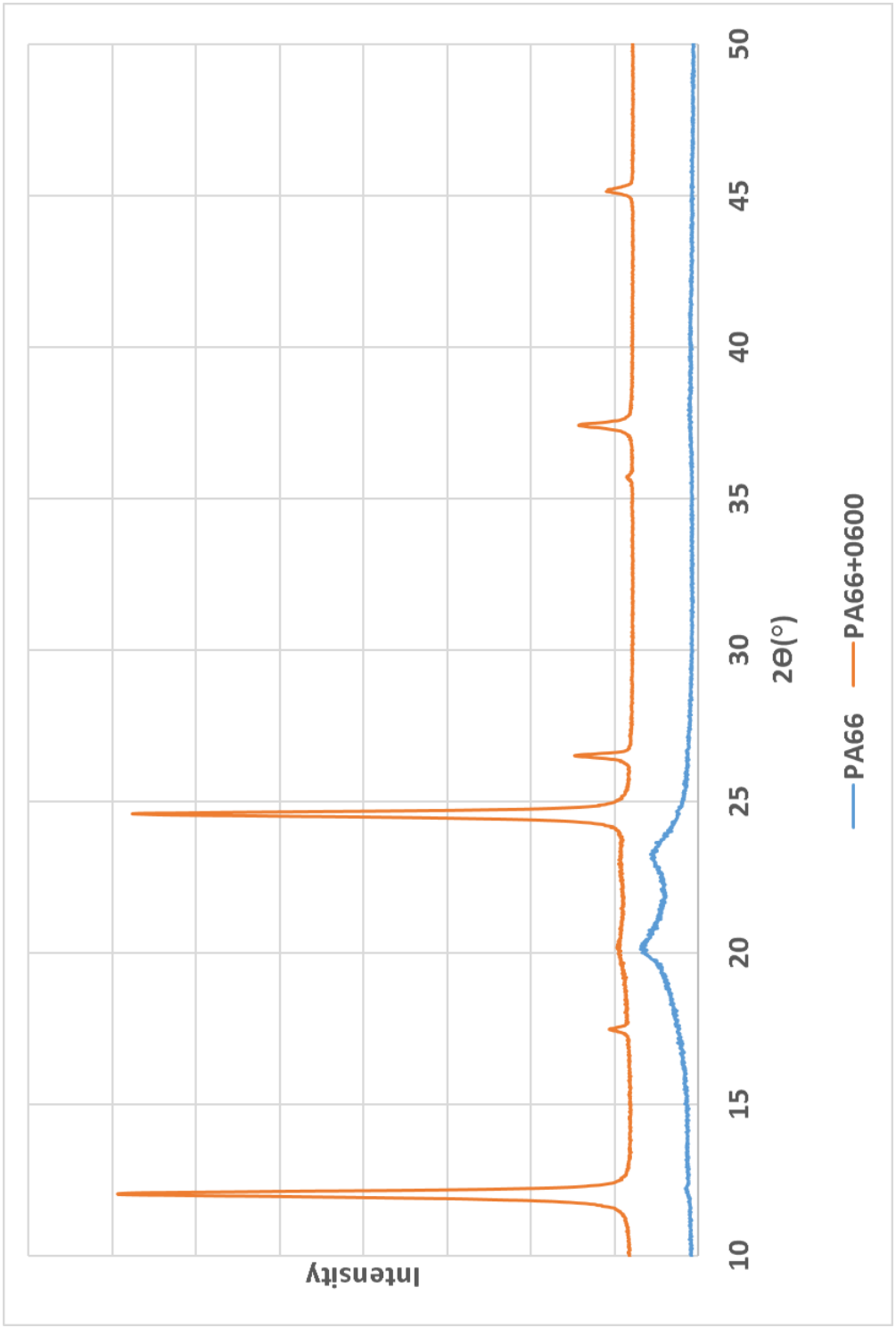

Figure 25 XRD patterns generated by nylon 6 6composites

1.22 Surface Morphology Using SEM

Although it is expected for a high aspect ratio like the XP15-0600 to be stronger due to lower agglomeration, in the SEM image taken at a fracture surface from the middle of an impact sample in Figure 26, it can be seen that there is still some agglomeration present. Figure 27 provides a closer view into the fracture. Although the XP15-0600 is a medium sized particle, it still falls in the nano particle domain and hence it can be hypothesized that there will always be some degree of agglomeration for such kaolin minerals. Due to the presence of a rough surface containing peaks, it can also be deduced that the sample deflected a lot of energy leading to such features.

Figure 28 shows the fracture surface from a Polarite 402A sample, which has a much finer particle size than XP15-0600. There is still some agglomeration as can be seen by the stacking of the effect and may explain the reduced tensile and flexural performance of Polarite 402A as compared to XP15-0600. Since the Polarite 402A has more than twice the impact energy of the XP15-0600, it can be confirmed using the mechanisms from the previous chapters that the finer particle size along with the smaller aspect ratio helps to improve impact performance. Furthermore, unlike the XP15-0600 sample, the Polarite 402A showcases a much smoother and flatter surface. This can be attributed to the fact that the sample absorbed most of the energy leading to a lower deflection and hence lower presence of peaks/ rough surface.

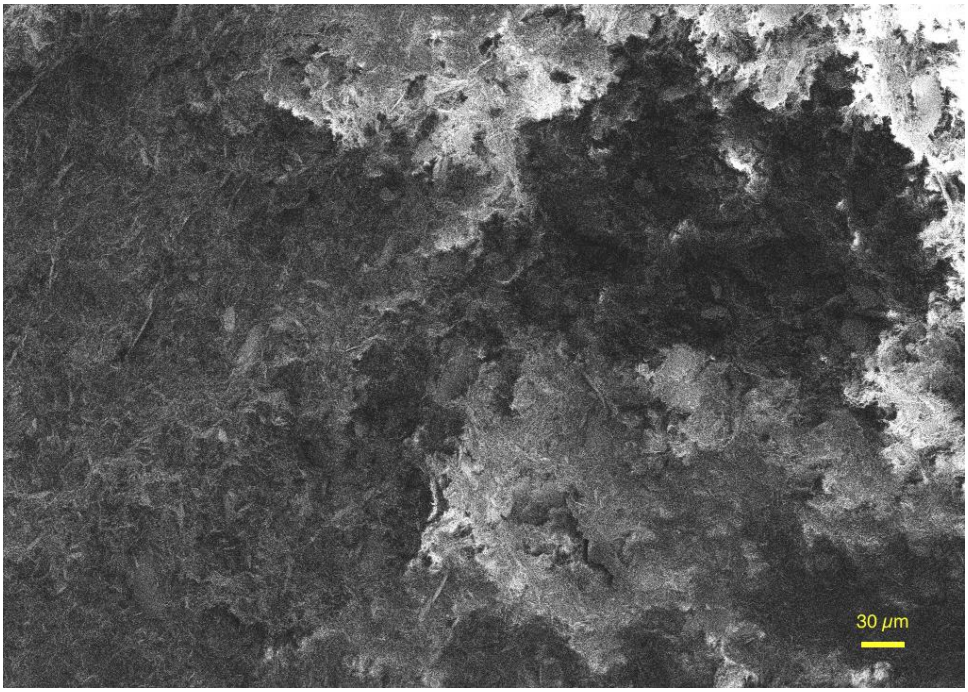

Figure 26 SEM image from the middle of an impact sample of PA66/XP15-0600 (70wt%/30wt%) sample showing the fracture surface

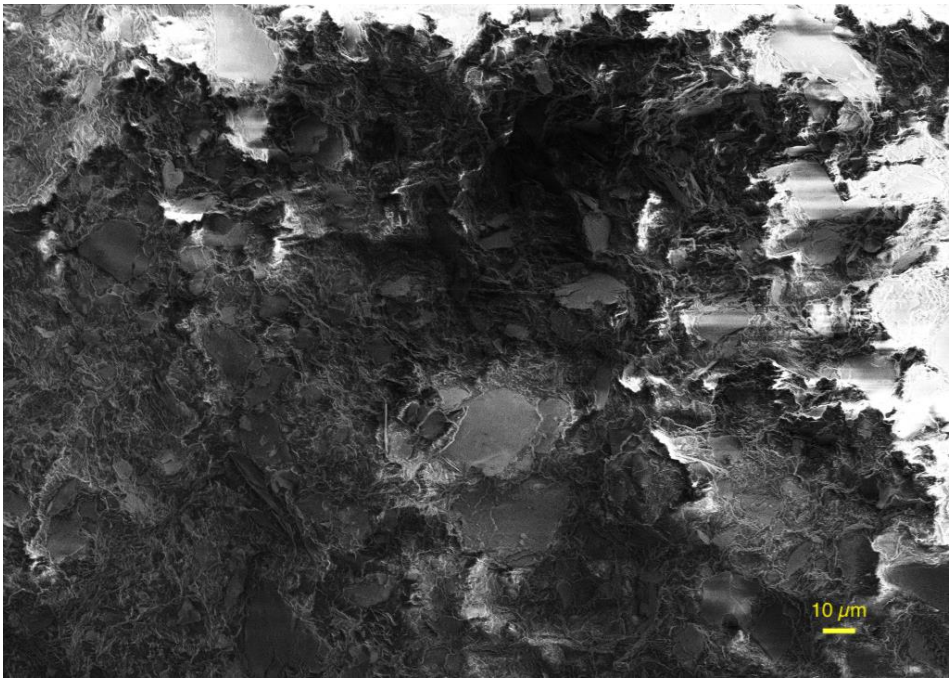

Figure 27 Higher magnification of impact sample of PA66/XP15-0600 (70wt%/30wt%) showing agglomeration of XP15-0600 particles

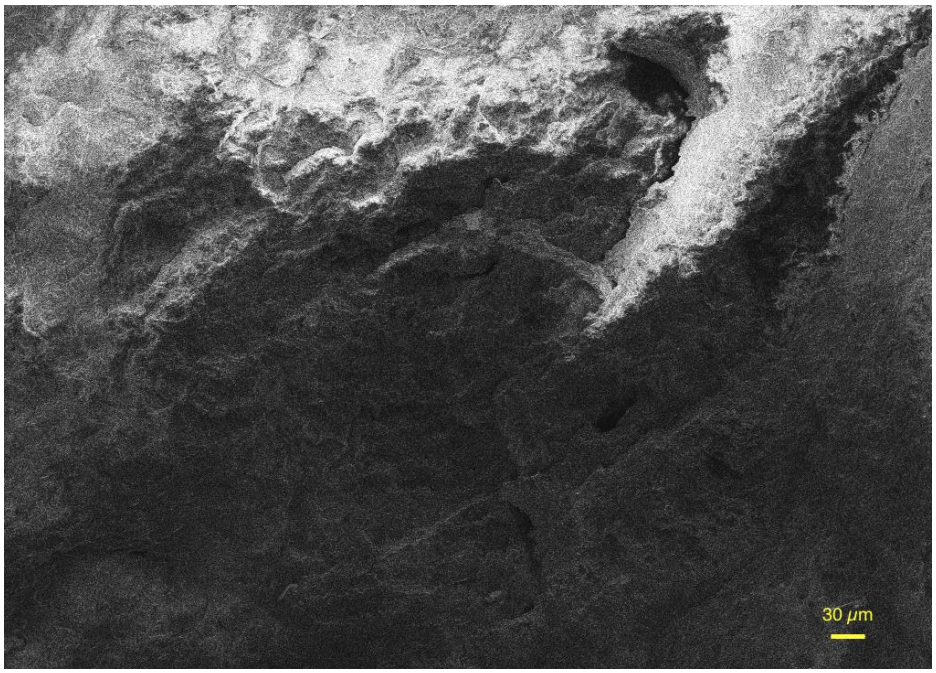

Figure 28 SEM image from middle of impact sample of PA66/Polarite 402A (70wt%/30wt%) fracture surface

1.23 Major Findings And Conclusion

Using kaolin minerals in a nylon 66 polymer matrix showed similar trends to the composites produced with nylon 6 as the base. The nylon 66 showed better performance in both tensile and impact but an inferior performance in flexural as compared to nylon 6 in percentage increase terms. The SEM, DSC and XRD data correlated positively with the data shown in the previous section with nylon 6 suggesting that the kaolins behave in a similar manner in both polymer matrices.

From an industry point of view, the results seen thus far are promising and can potentially allow manufacturers to use the kaolins in multiple polymers matrices and avail its benefits. Companies like Imerys should invest more in developing newer variation of kaolin that can be used in plastics.

SUMMARY, RECOMMENDATIONS AND FUTURE WORK

This thesis built upon Baioumy's prior research and further analyzed the use of surface treated nano kaolins in both nylon 6 and nylon 66 polymer matrices with the aim of eventually replacing glass fibers in such composites. The composites were produced on a lab scale using a twin screw micro extruder and an injection molding machine. Mechanical tests on the samples showed that although replacing glass fibers with kaolins does not produce as high tensile and flexural properties, they do produce higher impact energy. These results traced back to the size and aspect ratios of the kaolins and complied with the results obtain in Baioumy's studied, with finer particle sizes producing stronger tensile and flexural properties but lower impact properties. This study also analyzed pure mineral and polymer composites to better understand the varying effects of particle size and aspect ratio on the performance of the composite. The addition of kaolins to nylon 6 and nylon 66 showed a multifold increase in tensile, flexural and impact properties suggesting a strong potential use in multiple polymers bases. SEM was also employed to investigate the morphology of the filler and the dispersion in the matrix. The failure mechanisms in the samples corresponded to the one shown in Baioumy's study and included fiber pullouts, debonding and delamination, matrix cracking and fiber breakage while the kaolins exhibited some degree of agglomeration due to their small size.

From an industry point of view, the results from this study are promising and help to promote the idea of further research into kaolin minerals as fillers in composites. Additionally, there is research into new applications of kaolin, such as automobile brake

pads [Jide], which could further boost kaolin consumption and bring more business for companies like Imerys.

Some of the topics that can be further explored based on this study are:

- Evaluating the effects of different surface treatments of the kaolins on the mechanical properties of the composites
- Further exploring the effects of crystallinity of the composites and its effects on mechanical performance
- Performing thermal analysis on Nylon 66 composites to better understand if it would be more suitable for higher temperature applications
- Evaluate the effects of changing manufacturing parameters on the final properties of the composites
- Understand the effects of blending multiple kaolin minerals to further improve properties

APPENDIX A. DATA SHEETS FOR NYLON 6 AND NYLON 66

Product Information

Nov 2018

Ultramid® B3L
Polyamide 6

BASF
We create chemistry

Product Description

Ultramid B3L is an impact-modified, easy flowing injection molding PA6 grade for fast processing.

Applications

Typical applications include impact-resistant articles such as housings, fittings, small parts and anchors.

PHYSICAL	ASTM Test Method	Property Value	
Specific Gravity	D-792	1.1	
Mold Shrinkage (1/8" bar, in/in)		0.011	
Moisture, %	D-570		
(50% RH)		2.5	
(Saturation)		9	
MECHANICAL	**ASTM Test Method**	**Dry**	**Conditioned**
Tensile Strength, Yield, MPa (psi)	D-638		
23C (73F)		69 (10,000)	-
Elongation, Yield, %	D-638		
23C (73F)		4	-
Elongation, Break, %	D-638		
23C (73F)		25	-
Flexural Modulus, MPa (psi)	D-790		
23C (73F)		2,500 (362,000)	-
IMPACT	**ASTM Test Method**	**Dry**	**Conditioned**
Notched Izod Impact, J/M (ft-lbs/in)	D-256		
-40C (-40F)		53 (1.0)	-
23C (73F)		134 (2.5)	-
THERMAL	**ASTM Test Method**	**Dry**	**Conditioned**
Melting Point, C(F)	D-3418	220 (428)	-
Heat Deflection @ 264 psi (1.8 MPa) C(F)	D-648	66 (150)	-
Heat Deflection @ 66 psi (.45 MPa) C(F)	D-648	160 (320)	-
Coef. of Linear Thermal Expansion, mm/mm C (in/in F)	E-831	0.4 X10-4	-
UL RATINGS	**UL Test Method**	**Property Value**	
Flammability Rating, 0.4mm	UL94	HB	
Relative Temperature Index, 0.4mm	UL746B		
Mechanical w/o Impact, C		65	
Mechanical w/ Impact, C		65	
Electrical, C		65	
Flammability Rating, 0.8mm	UL94	HB	
Relative Temperature Index, 0.8mm	UL746B		
Mechanical w/o Impact, C		65	
Mechanical w/ Impact, C		65	
Electrical, C		65	

Product Information

DUPONT

Zytel®

nylon resin

Zytel® ST801 NC010A

Zytel® ST801 NC010A is a general purpose Super Tough nylon 66 resin. It offers outstanding impact resistance and high productivity.

Property	Test Method	Units	Value	
			50%RH	DAM
Mechanical				
Tensile Stress at 50% Strain	ISO 527-1/2	MPa		
50mm/min			39	
Yield Stress	ISO 527-1/2	MPa		
50mm/min			43	50
Nominal Strain at Break	ISO 527-1/2	%		
50mm/min			>50	32
Strain at Break	ISO 527-1/2	%		
50mm/min			>100	60
Yield Strain	ISO 527-1/2	%		
50mm/min			37	5,7
Tensile Modulus	ISO 527-1/2	MPa		
1mm/min			900	2000
Tensile Creep Modulus	ISO 899	MPa		
1000h			750	
1h			1200	
Notched Izod Impact	ISO 180/1A	kJ/m2		
-30C			20	20
23C			100	80
Notched Charpy Impact	ISO 179/1eA	kJ/m2		
-30C			17	18
23C			115	80
Unnotched Charpy Impact	ISO 179/1eU	kJ/m2		
-30C			NB	NB
23C			NB	NB

Properties measured at 23°C unless otherwise stated.
Please refer to the Safety Data Sheet, general guides and/or additional information about ventilation, handling, purging, drying, etc.

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APPENDIX B. MODEL FOR PREDICTING FLEXURAL MODULUS

A predictive model was built to determine the flexural modulus of a fiber reinforced composite without having to perform experimental testing. The thought process used to build this model is outlined in Figure 29.

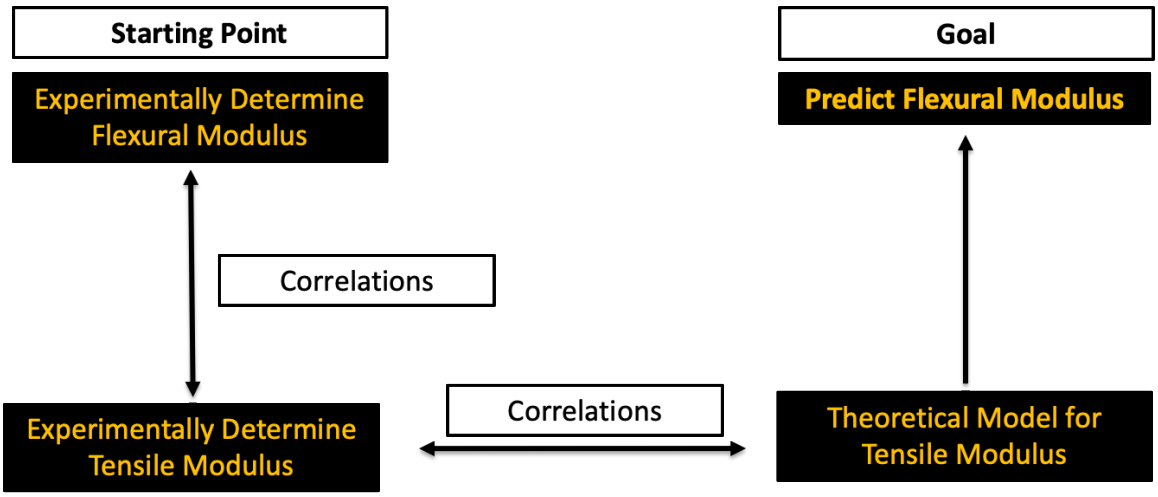


Figure 29 Flow diagram used to determine flexural modulus using theoretical values only

The model would begin by experimentally determining the flexural and tensile modulus of a composite with known composition (i.e. weight percentage of matrix and reinforcement). The correlation between the flexural and tensile modulus would be established and used to predict the flexural modulus of an unknown composite in a later step.

The results of the experimental tests would be compared with a theoretical model as presented in Mallick, Chapter 3 [Mallick, Chapter 3]. The model presented in Mallick establishes equations for tensile properties and hence a correlation factor between the experimental and theoretical tensile modulus can be found. Using this correlation factor, and the correlation between the tensile and flexural modulus, the flexural modulus of another composite can be predicted.

Mallick presents 2 models – one for unidirectional fibers and one for randomly oriented fibers. Since the composites produced in this thesis are injection molded, the material properties of the composite are likely to be somewhere between the two models. This can be showcased in Figure 30, which represents the degree of alignment of the fibers in injection molded parts. From the diagram, it is evident that randomly oriented fibers begin to align to a certain direction when injection pressure is applied in the mold.

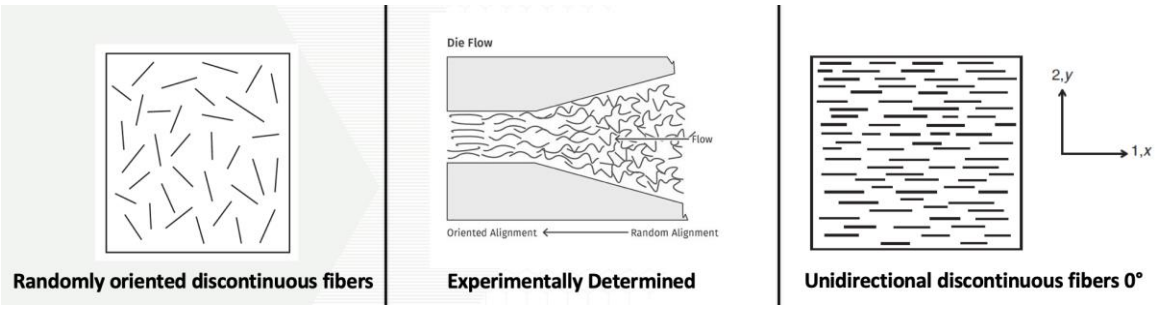


Figure 30 Orientation of fibers in models and experiments

Hence, the experimentally determined values were first compared to the two models to determine a correlation factor. Then, using the previously established correlation between the flexural and tensile modulus, the flexural modulus for a new composite can be predicted. The steps taken for this model are outlined below.

Assumptions:

- Randomly distributed fibers
- Matrix comprising of PA-6 and Mineral (82.4 wt% PA-6, 17.6 wt% Mineral (XP15-0600))
- High aspect ratio for fibers ≈ 2500
- $E_m \approx 4.75$ Gpa (from test data)
- $E_f \approx 81$ Gpa (from Owens Corning)

Equations used in the model [Mallick, Chapter 3]:

Unidirectional discontinuous fibers at 0°

Longitudinal modulus:

$$E_{11} = \frac{1 + 2(l_f/d_f)\eta_L v_f}{1 - \eta_L v_f} E_m,$$

Transverse modulus:

$$E_{22} = \frac{1 + 2\eta_T v_f}{1 - \eta_T v_f} E_m,$$

Shear modulus:

$$G_{12} = G_{21} = \frac{1 + \eta_G v_f}{1 - \eta_G v_f} G_m,$$

Major Poisson's ratio:

$$\nu_{12} = \nu_f v_f + \nu_m v_m,$$

Minor Poisson's ratio:

$$\nu_{21} = \frac{E_{22}}{E_{11}} \nu_{12},$$

where

$$\eta_L = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2(l_f/d_f)}$$
$$\eta_T = \frac{(E_f/E_m) - 1}{(E_f/E_m) + 2}$$
$$\eta_G = \frac{(G_f/G_m) - 1}{(G_f/G_m) + 1}$$

(B1 – B8)

Equations used for randomly oriented discontinuous fibers:

$$E_{\text{random}} = \frac{3}{8}E_{11} + \frac{5}{8}E_{22},$$

$$G_{\text{random}} = \frac{1}{8}E_{11} + \frac{1}{4}E_{22},$$

$$\nu_{\text{random}} = \frac{E_{\text{random}}}{2G_{\text{random}}} - 1.$$

(B9 - B11)

The values used in the model are shown in Table 13.

Table 13 Prediction model values

Property	**Value**	**Units**
l_f	25	mm
d_f	0.01	mm
v_f	0.052	
E_f	81	GPa
E_m	4.75	GPa

Where l_f is the fiber length, d_f is the fiber diameter, v_f is the fiber volume fraction, E_f is the fiber modulus and E_m is the matrix modulus. The volume fraction was obtained using the values in Table 14 and equation B12.

Table 14 Weight fraction and density of matrix and fiber

w_f	0.15
ρ_f	2.54
ρ_m	1.27

$$v_f = \frac{\frac{w_f}{\rho_f}}{\frac{w_f}{\rho_f}+\frac{(1-w_f)}{\rho_m}} \quad \text{B12}$$

Where w_f is the weight fraction, ρ_f is the density of the fibers (g/cm^3) and ρ_m is the density of the matrix (g/cm^3). The density of the matrix was obtained using the rule of mixtures with the density of kaolin taken as 2.65 g/cm^3 (8.4 volume %) and the density of nylon 6 taken as 1.14 g/cm^3 (91.6 volume %).

Using these equations and values, the data shown in Table 15 was obtained.

Table 15 Comparison of experimental and model results formukation

E_{random} (from model)	6.64 GPa
$E_{tensile}$ (from experiment)	7.55 GPa
E_{11} (from model)	8.70 GPa

From this data, it was concluded that the values obtained experimentally were approximately halfway between those obtained using the random and unidirectional models (with a slight bias towards the random model). Hence, using the E_{random} as a base, the correlation factor can be determined as

$$\frac{E_{tensile}}{E_{random}} = \frac{7.55}{6.64} = 1.185 \quad \text{(B13)}$$

Similarly, to obtain a correlation factor between the flexural modulus and the tensile modulus, the following operation was performed

$$\frac{E_{flexural}}{E_{tensile}} = \frac{5.65}{7.55} = 0.74 \quad \text{(B14)}$$

8

Therefore, using the model described above and the correlation factors B13 and B14, one can determine the flexural modulus of an untested composite. The process flow can be seen in Figure 31.

$$E_{random}(from\ model) \times 1.185 = E_{tensile}$$

$$\downarrow$$

$$E_{tensile} \times 0.74 = E_{flexural}$$

Figure 31 Obtaining flexural modulus from model

However, this model does have a few flaws. Primarily this model does not consider the vast range of effects the different features of the filler material have on the composite (i.e. surface treatment, particle size, aspect ratio). Since many kaolin fillers can have the same density while having different properties, this model may fail to make accurate predictions. This model also only works for composites where the reinforcement is a fiber. Since many of the experiments performed in this thesis did not contain fiber reinforcements, this model was subsequently dropped and not used for analysis. This model can be further improved by performing an error analysis between the predicted values and the experimental results. The model presented here assumed a linear relationship between the tensile and flexural modulus. A better correlation factor could be established by performing additional tests and finding a model, such as quadratic or exponential, that fits the results better.

APPENDIX C. DENSITY ANALYSIS TO DETERMINE WEIGHT PERCENT OF NYLON AND KAOLIN

In order to confirm the weight percentages of the final composites produced, a density analysis was performed. 7 random formulations were picked and the density of 3 samples from each formulation was determined using the water displacement test. The results are shown in Table 16. The formula used to calculate the density is shown in equation C1.

$$Density = \frac{Sample\ Mass}{Sample\ Mass - Water\ Mass} \times 0.997$$

Table 16 Determining weight percentage of Nylon 6 using density analysis

XP15-0600	Mass (g)	Water Mass (g)	Density (g/cm3)	Volume percentage	Weight Percentage
1	1.7633	0.4627	1.355758881	86%	72%
2	1.7916	0.4679	1.353478885	86%	72%
3	1.7687	0.4591	1.350565058	86%	73%

XP15-0006	Mass (g)	Water Mass (g)	Density (g/cm3)	Volume percentage	Weight Percentage
1	1.6522	0.3719	1.290478794	90%	80%
2	1.5916	0.364	1.296513522	90%	79%
3	1.6244	0.3425	1.267181527	92%	82%
Polarite 102A	**Mass (g)**	**Water Mass (g)**	**Density (g/cm3)**	**Volume percentage**	**Weight Percentage**
1	1.8957	0.5031	1.361266695	85%	71%
2	1.8135	0.4849	1.364970646	85%	71%
3	1.7006	0.4585	1.36913292	85%	71%
Polarite 402A	**Mass (g)**	**Water Mass (g)**	**Density (g/cm3)**	**Volume percentage**	**Weight Percentage**
1	1.7721	0.4711	1.362106072	85%	71%

2	1.7715	0.477	1.368482039	85%	71%
3	1.7232	0.4635	1.367944749	85%	71%
XP15-0621	**Mass (g)**	**Water Mass (g)**	**Density (g/cm3)**	**Volume percentage**	**Weight Percentage**
1	1.7038	0.4359	1.343796829	87%	73%
2	1.8912	0.4971	1.356574134	86%	72%
3	1.868	0.4805	1.346306306	86%	73%
Hydrite SB60	**Mass (g)**	**Water Mass (g)**	**Density (g/cm3)**	**Volume percentage**	**Weight Percentage**
1	1.8104	0.4736	1.354278875	86%	72%
2	1.8525	0.459	1.329386437	87%	75%
3	1.8005	0.4662	1.349396687	86%	73%

Translink	Mass (g)	Water Mass (g)	Density (g/cm3)	Volume percentage	Weight Percentage
1	1.6993	0.4634	1.37494943	84%	70%
2	1.8262	0.4931	1.369889731	85%	71%
3	1.7041	0.4555	1.364808586	85%	71%

The results from the weight percentage analysis show that the composition of the final composite was, in general, similar to the formulation that was put into the compounder (70 wt% nylon, 30 wt% kaolin). The deviation observed in XP15-0006 can be attributed to incorrect mixing of the formulation or possibly due to the lower density of the kaolin which affected the calculated value.

APPENDIX D. USING A DOE TO UNDERSTAND THE EFFECTS OF KAOLIN PROPERTIES

To understand the relative effects of the kaolin properties studied in this thesis (surface treatment, particle size, aspect ratio), a design of experiments analysis was conducted.

The DOE was conducted using the JMP Pro software. The initial step was to define the responses of the experiment. The values chosen for the responses were Tensile Strength, Tensile Modulus, Flexural Strength, Flexural Modulus and Impact Strength, since these were the key properties of the kaolins being evaluated in this thesis.

The factors chosen for the experiment were Surface Treatment (Treated vs Non-Treated), Particle Size (Fine, Medium, Large) and Aspect Ratio (Negligible, Medium, Large), since these were the properties of the kaolin.

Using the responses and factors, the experiment was set up as shown in Table 17.

Table 17 Model for design of experiment

Run	Surface Treatment	Particle Size	Aspect Ratio
1	Treated	Fine	Large
2	Treated	Large	Negligible
3	Treated	Medium	Large
4	Untreated	Fine	Large
5	Untreated	Fine	Negligible
6	Untreated	Large	Large
7	Treated	Medium	Medium
8	Treated	Large	Large
9	Treated	Fine	Negligible
10	Untreated	Medium	Negligible
11	Untreated	Fine	Large
12	Untreated	Large	Medium

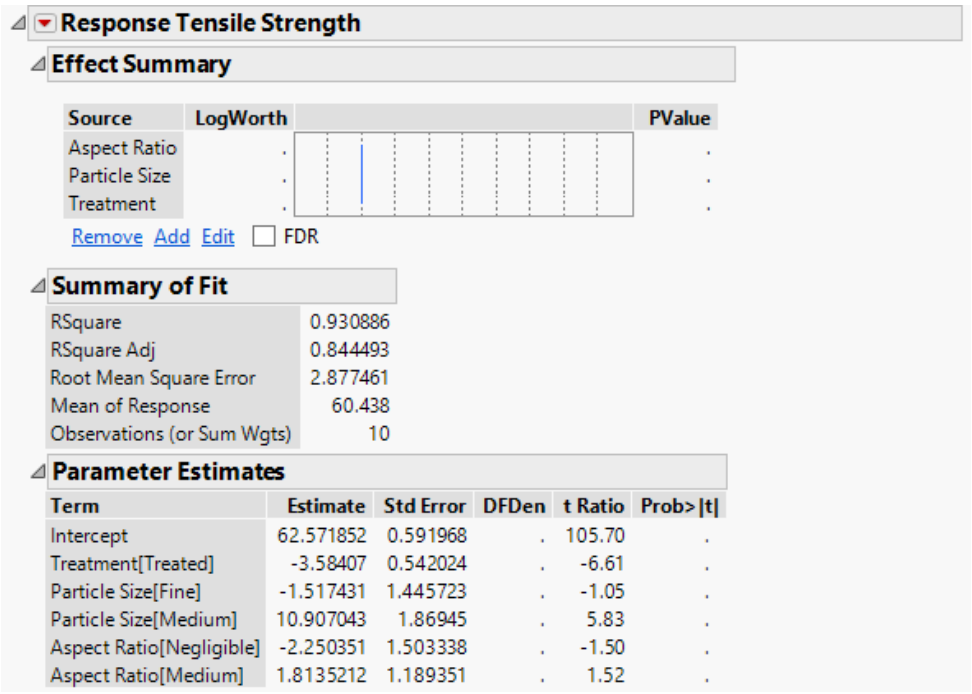
Using these parameters, the values obtained from the experimental results were put into the model as shown in Table 18.

Table 18 Experimental values used for DOE runs

	Tensile Strength (MPa)	**Tensile Modulus (MPa)**	**Flexural Strength (MPa)**	**Flexural Modulus (MPa)**	**Impact Strength (kJ/m^2)**
1	55.28	3502.89	125.84	5662	8.41
2	49.19	2326	82.11	2090	6.06
3	71.02	6233.71	152.97	7360	7.76
4	67.31	5758.75	146.07	6810	7.3
5	59.96	4454.27	134.78	5803	7.44
6	57.25	5379.59	133.88	6355	6.83
7	71.02	6233.71	152.97	7360	7.76
8	49.19	2326	82.11	2090	6.06
9	56.85	2661.56	99.13	3047	10.76
10	-	-	-	-	-
11	67.31	5758.75	146.07	6810	7.3
12	-	-	-	-	-

Since not all possible combinations of the properties were available in the kaolins used in this thesis, there were some values which were left blank, as shown in run 10 and run 12. Some values were also repeated for the same reasons as in runs 3,7 and 4,11.

From these results, a Standard least Squares model was run on JMP to evaluate the effect of each factor on the responses. The results are shown in Figure 32 through 36.



Response Tensile Strength

Effect Summary

Source	LogWorth	PValue
Aspect Ratio	.	.
Particle Size	.	.
Treatment	.	.

Remove Add Edit ☐ FDR

Summary of Fit

RSquare	0.930886
RSquare Adj	0.844493
Root Mean Square Error	2.877461
Mean of Response	60.438
Observations (or Sum Wgts)	10

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|
Intercept	62.571852	0.591968	.	105.70	.
Treatment[Treated]	-3.58407	0.542024	.	-6.61	.
Particle Size[Fine]	-1.517431	1.445723	.	-1.05	.
Particle Size[Medium]	10.907043	1.86945	.	5.83	.
Aspect Ratio[Negligible]	-2.250351	1.503338	.	-1.50	.
Aspect Ratio[Medium]	1.8135212	1.189351	.	1.52	.

Figure 32 Effect in tensile strength

Response Tensile Modulus

Effect Summary

Source	LogWorth	PValue
Particle Size	1.561	0.02745
Treatment	1.137	0.07291
Aspect Ratio	0.075	0.84071

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Summary of Fit

RSquare	0.963551
RSquare Adj	0.91799
Root Mean Square Error	422.9896
Mean of Response	4463.523
Observations (or Sum Wgts)	10

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|
Intercept	4985.1374	245.6296	1.251	20.30	0.0158*
Treatment[Treated]	-1142.216	163.44	1.125	-6.99	0.0729
Particle Size[Fine]	-810.519	289.4147	3.516	-2.80	0.0565
Particle Size[Medium]	2152.9234	454.5988	3.914	4.74	0.0096*
Aspect Ratio[Negligible]	-475.7301	429.6798	3.963	-1.11	0.3309
Aspect Ratio[Medium]	124.69473	741.9403	1.88	0.17	0.8829

Figure 33 Effect of factors on tensile modulus

Response Flexural Strength

Effect Summary

Source	LogWorth	PValue
Particle Size	1.517	0.03040
Treatment	1.249	0.05640
Aspect Ratio	0.692	0.20339

Remove Add Edit ☐ FDR

Summary of Fit

RSquare	0.976135
RSquare Adj	0.946305
Root Mean Square Error	7.333057
Mean of Response	125.593
Observations (or Sum Wgts)	10

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|
Intercept	133.46321	5.016207	2.783	26.61	0.0002*
Treatment[Treated]	-16.48893	4.323914	2.131	-3.81	0.0564
Particle Size[Fine]	-3.391685	4.712728	2.6	-0.72	0.5309
Particle Size[Medium]	30.093186	6.908323	2.683	4.36	0.0280*
Aspect Ratio[Negligible]	-11.80509	6.450436	2.844	-1.83	0.1697
Aspect Ratio[Medium]	9.2603571	10.36309	3.2	0.89	0.4336

Figure 34 Effect of factors on flexural strength

Response Flexural Modulus

Effect Summary

Source	LogWorth	PValue
Particle Size	1.148	0.07118
Treatment	1.014	0.09689
Aspect Ratio	0.665	0.21631

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Summary of Fit

RSquare	0.959821
RSquare Adj	0.909597
Root Mean Square Error	722.4495
Mean of Response	5338.7
Observations (or Sum Wgts)	10

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|
Intercept	5928.1253	494.4298	2.777	11.99	0.0018*
Treatment[Treated]	-1217.19	426.0257	2.124	-2.86	0.0969
Particle Size[Fine]	-256.275	464.6122	2.595	-0.55	0.6251
Particle Size[Medium]	2083.4849	681.2156	2.678	3.06	0.0638
Aspect Ratio[Negligible]	-1131.16	636.2021	2.84	-1.78	0.1786
Aspect Ratio[Medium]	893.88532	1022.561	3.197	0.87	0.4427

Figure 35 Effect of factors on flexural modulus

Response Impact Strength

Effect Summary

Source	LogWorth	PValue
Particle Size	0.540	0.28819
Treatment	0.260	0.54968
Aspect Ratio	0.031	0.93136

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Summary of Fit

RSquare	0.34623
RSquare Adj	-0.47098
Root Mean Square Error	1.388421
Mean of Response	7.568
Observations (or Sum Wgts)	10

Parameter Estimates

Term	Estimate	Std Error	DFDen	t Ratio	Prob>|t|
Intercept	7.5278935	0.814595	0.583	9.24	0.1718
Treatment[Treated]	0.4699454	0.477211	0.724	0.98	0.5497
Particle Size[Fine]	1.1903025	0.982586	3.79	1.21	0.2958
Particle Size[Medium]	-0.25691	1.586922	3.93	-0.16	0.8794
Aspect Ratio[Negligible]	-0.038141	1.50764	3.127	-0.03	0.9813
Aspect Ratio[Medium]	0.6075874	2.665664	0.507	0.23	0.8796

Figure 36 Effect of factors on impact strength

In the results from the DOE, the particle size seemed to have had the largest effect on the responses. This can be seen from the effect summary of each of the responses. This also agrees with some of the results obtained in this thesis where particle size of the kaolin seemed to have a great effect on the mechanical properties of the composite. The results from this DOE, however, are not very strong since many of the estimated parameters are negative which indicate that the data was insufficient to make an accurate prediction. This DOE can be further enhanced by conducting more trials with a greater range of combination of the factors.

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